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Wastes from Manufacture of Dyes and Pigments. Volume 4. Anthraquinone Dyes and Pigments

SRI International, Menlo Park, CA

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WASTES FROM MANUFACTURE OF DYES AND PIGMENTS: VOLUME 4. ANTHRAQUINONE DYES AND PIGMENTS

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A preliminary study of the manufacture of Anthraquinone dyes and pigments was conducted to determine if process waste streams might contain hazardous material. The study first identifies the dyes and pigments that belong to this segment of the industry, the amounts produced and the known U.S. producers. The chemistry of these dyes and pigments is discussed as well as the overall production process and waste treatment practices. Several waste streams that could contain hazardous material are identified and seven companies that produce representative dyes and pigments are recommended for a sampling program to confirm the composition and amounts of these waste streams.

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report is one of a series of preliminary studies of segments of the dye and pigment manufacturing industry conducted for the Organic and Inorganic Chemicals and Products Branch of the Industrial Pollution Control Division. The objective of these studies was to determine if process waste streams might contain hazardous material and to recommend sites where a sampling program could be used to confirm the nature of any hazards that were identified.

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ABSTRACT

A preliminary study of the manufacture of Anthraquinone dyes and pigments was conducted to determine if process waste streams might contain hazardous material. The study first identifies the dyes and pigments that belong to this segment of the industry, the amounts produced and the known U.S. producers. The chemistry of these dyes and pigments is discussed as well as the overall production process and waste treatment practices. Several waste streams that could contain hazardous material are identified and seven companies that produce representative dyes and pigments are recommended for a sampling program to confirm the composition and amounts of these waste streams.

This report is submitted in fulfillment of Contract No. 68-03-2944 by SRI International under the sponsorship of the U.S. Environmental Protection Agency. The report covers the period July 1981 to December 1981, and work was completed as of July 31, 1983.

CONTENTS

FOREWORD iii

ABSTRACT iv

TABLES vi

1. INTRODUCTION 1

2. SUMMARY AND CONCLUSIONS 11

3. PROCESS CHEMISTRY 13

- Introduction 13
- Synthesis of the Anthraquinone Ring 14
- Preparation of Substituted Anthraquinones 15
- Anthraquinone Acid Dyes 19
- Anthraquinone Disperse Dyes 22
- Anthraquinone Pigments and Mordant Dyes 24
- Anthraquinone Vat Dyes 26

4. DYE INTERMEDIATES 35

5. SOURCES OF WASTE DISCHARGES DURING DYE AND PIGMENT MANUFACTURING 44

- Overview of Dye and Pigment Production Processes 44
- Raw Material Receiving and Handling 48
- Dye Synthesis 49
- Product Filtration 51
- Drying, Grinding, Standardization, Blending, and Packaging 52
- Wastewater Treatment 53

6. MATERIAL IN THE WASTE STREAMS FROM ANTHRAQUINONE DYE AND PIGMENT PRODUCTION 58

REFERENCES 74

TABLES

Number		Page
1.	Anthraquinone Dyes and Pigments Included in This Study.....	2
2.	Anthraquinone Dyes and Pigments of Known 1978 U.S. Commercial Production (greater than 20 metric tons per year).....	10
3.	Organic Intermediates and Chemical Reagents Used to Produce Anthraquinone Dyes and Pigments (with Known 1978 Commercial Production Greater than 20 Metric Tons)	36
4.	Organic Intermediates and Chemical Reagents Used to Produce Anthraquinone Dyes and Pigments.....	39
5.	Material Requirements for Production of Some Anthraquinone Dyes and Pigments.....	47
6.	Hazardous Wastes that may result from Anthraquinone Dye and Pigment Production.....	50
7.	A Partial List of Compounds Found by Games and Hites (1977) in the Composite Samples Collected from a Dye Manufacturing Plant.....	54
8.	Organic Materials that May Appear in the Waste Streams from the Production of Anthraquinone Dyes and Pigments of Known 1978 U.S. Commercial Production Greater than 20 metric tons.....	61
9.	Directory of Dye and Organic Pigment Manufacturers, 1978.....	64
10.	1978 Producers of Anthraquinone Dyes and Pigments.....	65
11.	Organic Solvents Used in Anthraquinone Dye and Pigment Manufacturing and the Dyes and Pigments Known To Be Associated with Their Use.....	72

SECTION 1

INTRODUCTION

The Resource Conservation and Recovery Act (RCRA) requires that hazardous solid wastes produced by manufacturing operations be identified and disposed in a manner that limits the release of hazardous materials to the environment. To date, many specific waste streams from manufacturing processes have been listed in regulations as being hazardous because of their chemical composition. The objective of this study is to determine if wastes produced by the manufacture of dyes and pigments in the United States require listing as hazardous materials. An analysis of both the chemistry and the physical processing involved in dye and pigment manufacturing is used to identify all wastes that may contain significant chemical hazards. An analysis of the industry is used to determine specific manufacturers where the candidate wastes may be produced. This information will allow contractors of the U.S. Environmental Protection Agency to design a sampling and analysis program to confirm or disprove the presence of hazardous materials in the candidate wastes and thereby develop a basis for listing dye and pigment manufacturing wastes under RCRA. This report deals with the wastes from the manufacture of anthraquinone dyes and pigments.

In 1972, production of 21,200 metric tons for all anthraquinone dyes was reported to the U.S. Tariff Commission (1974). This represented 18% of the total reported dye production of 120,000 metric tons for that year. Anthraquinone dyes (and pigments) represented the second largest structural class of dyes based on U.S. production volume. Data on U.S. production by structural class have not been reported since 1972. An industry contact* indicated that during the last few years, U.S. commercial production of anthraquinone dyes has decreased significantly.

Although more than 800 anthraquinone dyes and pigments are listed in the Colour Index (The Society of Dyers and Colourists, 1980), fewer than 300 of these are currently imported or produced in commercially significant quantities in the United States. Table 1 gives U.S. production data for the 145 commercially significant anthraquinone dyes and pigments--dyes produced at levels greater than 2.3 metric tons in 1978 and pigments produced at levels greater than 0.5 metric tons. These 1978 U.S. production levels were taken

*A. Stein, E. I. Dupont de Nemours and Co., Inc., Dec. 1981, Personal communication.

Table 1

ANTHRAQUINONE DYES AND PIGMENTS
INCLUDED IN THIS STUDY

C.I No.	C.I. Name	1978 U.S. Commercial Production (metric tons/yr)	Concentration of the Dye in the Commercial Product (wt%)
58000	Mordant Red 11	>2	lake[b]
58000[a]	Pigment Red 83	33	lake
58055	Pigment Violet 5:1	46	toner[c]
58825	Vat Green 7	>2	
59100	Vat Yellow 4	>2	12.5
59105	Vat Orange 1	>7	20
59300	Pigment Red 168	>1	toner
59300	Vat Orange 3	>2	13.5
59700	Vat Orange 9	>5	12
59700	Pigment Orange 40	>0.5	toner
59705	Vat Orange 2	335	12
59710	Vat Orange 4	>2	6
59710	Pigment Red 216	> 0.5	toner
59800	Vat Blue 20	>5	14
59800	Pigment Blue 65	>0.5	toner
59805	Vat Blue 19	>2	

[a] Mordant Red 11 and Pigment Red 83 have the same chemical structure; therefore they are given the same C.I. No. The different names refer to the commercial form of the product, e.g., a vat dye, pigment, or mordant dye. It is common in this class of dyes and pigments for the same chemical to be sold as a vat dye and a pigment or as a mordant dye and a pigment or as a disperse dye and a solvent dye.

[b] A lake is an organic pigment produced by the interaction of an oil-soluble organic dye, a precipitant, and an absorptive inorganic substrate.

[c] A toner is an organic pigment that does not contain inorganic pigment, precipitant, or an adsorptive inorganic substrate.

Table 1 (Continued)

C.I. No.	C.I. Name	1978 U.S. Commercial Production (metric tons/yr)	Concentration of the Dye in the Commercial Product (wt%)
59815	Vat Blue 18	>7	13
59825	Vat Green 1	>7	6
59850	Vat Green 9	>7	12.5
59855	Vat Black 16	>2	
60005	Vat Violet 9	>7	12
60005	Pigment Violet 33	>0.5	toner
60010	Vat Violet 1	>5	11
60010	Pigment Violet 31	>1	toner
60505	Solvent Red 111	>5	
60505	Disperse Red 9	>2	
60710	Disperse Red 15	>7	
60710	Solvent Red 53	>2	
60724	Disperse Violet 27	23	
60725	Solvent Violet 13	>2	
60725	Disperse Blue 72	> 2	
60730	Acid Violet 43	>2	
60755	Disperse Red 4	35	
60756	Disperse Red 60	656	
60767	Disperse Blue 27	>2	
61100	Solvent Violet 11	>2	
61100	Disperse Violet 1	>23	
61102	Disperse Violet 28	>5	
61111	Basic Blue 47	>2	
61125	Acid Blue 23	>2	
61200	Reactive Blue 19	>2	
61205	Reactive Blue 4	>2	
61205:1	Reactive Blue 5	>2	

Table 1 (Continued)

C.I. No.	C.I. Name	1978 U.S. Commercial Production (metric tons/yr)	Concentration of the Dye in the Commercial Product (wt%)
61505	Disperse Blue 3	630	
61512	Basic Blue 22	>2	
61525	Solvent Blue 11	>2	
61530	Acid Blue 27	>7	
61551	Disperse Blue 134	>2	
61551	Solvent Blue 36	>5	
61552	Solvent Blue 59	>5	
61554	Solvent Blue 35	>2	
61565	Solvent Green 3	>5	
61570	Acid Green 25/95[d]	>11	
61585	Acid Blue 80	>2	
61705	Solvent Violet 14	>2	
62015	Disperse Red 11	>5	
62015	Solvent Violet 26	>2	
62025	Disperse Violet 26/31[e]	>2	
62045	Acid Blue 62	>2	
62055	Acid Blue 25	>14	
62070	Acid Blue 145	>5	
62073	Acid Blue 230	>2	
62105	Acid Blue 78	>7	
62125	Acid Blue 40	408	
62130	Acid Blue 41/71[f]	>5	
62175	Disperse Red 86	150	
62500	Disperse Blue 7	>5	
62500	Solvent Blue 69	>2	

[d]The dye C.I. 61570 is known as C.I. Acid Green 25 and C.I. Acid Green 95; however, it is marketed as Acid Green 25.

[e]The dye C.I. 62025 is known as C.I. Disperse Violet 26 and C.I. Disperse Violet 31.

[f]The dye C.I. 62130 is known as C.I. Acid Blue 41 and C.I. Acid Blue 71. In 1978 both were marketed.

Table 1 (Continued)

C.I. No.	C.I. Name	1978 U.S. Commercial Production (metric tons/yr)	Concentration of the Dye in the Commercial Product (wt%)
62560	Acid Green 41	>2	
63000	Acid Blue 43	>2	
63010	Acid Blue 45	>2	
63265	Disperse Blue 73	>5	
63285	Disperse Blue 56	>2	
63615	Mordant Black 13	>2	
65300	Pigment Red 177	>2	
65429	Vat Yellow 33	>2	15
67000	Vat Red 10	>2	18
67300	Vat Yellow 2	>7	8.5
68700	Vat Violet 13	>5	6.25
69005	Vat Black 27	>7	12.5
69015	Vat Brown 3	108	11
69015	Pigment Brown 28	>0.5	toner
69025	Vat Orange 15	80	10
69500	Vat Green 3	393	10
69525	Vat Black 25	1036	12.5
69800	Pigment Blue 60	>0.5	toner
69800	Vat Blue 4	>2	
69810	Pigment Blue 22	>1	toner
69810	Vat Blue 14	>2	
69825	Vat Blue 6	495	8.33
69825	Pigment Blue 64	>0.5	toner
70150	Disperse Yellow 77	>2	
70320	Vat Red 13	>2	11
70320	Pigment Red 195	>0.5	toner
70600	Pigment Yellow 24	>0.5	toner
70600	Vat Yellow 1	>2	
70800	Vat Brown 1	>7	11
71050	Vat Green 8	>2	8.5
71100	Vat Red 15	>5	

Table 1 (Continued)

C.I. No.	C.I. Name	1978 U.S. Commercial Production (metric tons/yr)	Concentration of the Dye in the Commercial Product (wt%)
71100	Pigment Red 194	>0.5	
71105	Vat Orange 7	>5	11
71105	Pigment Orange 43	>1	toner
71110	Vat Red 14	>2	20
71120	Vat Brown 14	>2	12
71127	Pigment Red 224	>0.5	toner
71130	Vat Red 23	>2	
71130	Pigment Red 179	>0.5	toner
71135	Vat Red 32	>5	20
71135	Pigment Red 189	>0.5	toner
71137	Pigment Red 149	>0.5	toner
71140	Vat Red 29	>2	
71140	Pigment Red 190	>1	toner
71145	Pigment Red 123	>1	toner
71200	Vat Blue 16	>2	16
-	Acid Blue 277	>2	
-	Acid Blue 298	>2	
-	Basic Blue 21	>2	
-	Basic Blue 35	>2	
-	Basic Blue 45	>2	
-	Basic Blue 60	>5	
-	Basic Blue 94	>2	
-	Disperse Blue 55	>2	
-	Disperse Blue 60	>5	
-	Disperse Blue 62	>5	
-	Disperse Blue 64	294	
-	Disperse Blue 77	>5	
-	Disperse Blue 81	>2	
-	Disperse Blue 87	>2	

Table 1 (Continued)

C.I. No.	C.I. Name	1978 U.S. Commercial Production (metric tons/yr)	Concentration of the Dye in the Commercial Product (wt%)
-	Disperse Blue 95	> 2	
-	Disperse Blue 109	> 2	
-	Disperse Blue 112	> 2	
-	Disperse Blue 118	> 2	
-	Disperse Blue 192	> 2	
-	Disperse Green 7	> 2	
-	Disperse Red 55	254	
-	Disperse Red 59	29	
-	Disperse Red 91	> 2	
-	Disperse Red 92	> 2	
-	Disperse Red 133	> 2	
-	Disperse Red 138	> 2	
-	Disperse Red 159	> 2	
-	Disperse Red 178	> 2	
-	Disperse Red 217	> 2	
-	Disperse Red 263	> 5	
-	Disperse Violet 17	> 2	
-	Disperse Violet 36	> 2	
-	Disperse Violet 41	> 2	
-	Disperse Violet 64	> 2	
-	Disperse Violet 81	> 2	
-	Reactive Blue 29	> 2	
-	Solvent Blue 16	> 2	
-	Solvent Blue 58	> 2	
-	Solvent Blue 98	>2	
-	Solvent Red 168	>2	
-	Vat Black 14	>2	11
-	Vat Black 21	>2	18.5
-	Vat Black 22	>5	19

Table 1 (Concluded)

C. I. No.	C. I. Name	1978 U.S. Commercial Production (metric tons/yr)	Concentration of the Dye in the Commercial Product (wt%)
-	Vat Blue 66	>2	
-	Vat Brown 11	>2	12
-	Vat Brown 13	>2	17
-	Vat Green 32	>2	
-	Vat Violet 21	>2	
-	Vat Yellow 15	>2	11.5
-	Vat Yellow 22	>2	10

from the Organic Dyes and Pigments Data Base, prepared by SRI International (Swett, et al., 1983). For some dyes and pigments, production is shown only as greater than a minimum number. These are dyes and pigments produced by fewer than three manufacturers or by three or more where one or two dominate the market. Public sources do not list specific production amounts in these cases. Production data are for the commercial product, which may include solvents, other diluents, and impurities in addition to the specific dye chemical of interest; concentration of the dye in the commercial product may vary from 6% to 100% and is given in Table 1, if available. The table is arranged according to the Colour Index (C.I.) number.

Of the 145 commercially significant anthraquinone dyes and pigments that are produced in the United States and listed in Table 1, only 18 are known to have 1978 U.S. commercial production of greater than 20 metric tons. The commercial production data for these dyes are listed in Table 2. These 18 dyes and pigments represent a combined U.S. commercial production in 1978 of 5,030 metric tons. Each of these dyes and pigments are produced by at least three manufacturers. It usually requires several manufacturers to produce a dye of commercial consequence, because of the relatively small batch production operations (Steadman et al., 1977). It also might be conjectured that if a dye becomes notable in the market, several manufacturers would be capable of producing the dye. Of the remaining 127 anthraquinone dyes and pigments listed in Table 1 and not included in Table 2 as being major dyes and pigments, only the following 11 are reported to be produced by at least three manufacturers:

C.I. 59105 C.I. Vat Orange 1
C.I. 59815 C.I. Vat Blue 18
C.I. 59825 C.I. Vat Green 1
C.I. 59850 C.I. Vat Green 9
C.I. 60710 C.I. Disperse Red 15
C.I. 61530 C.I. Acid Blue 27
C.I. 62055 C.I. Acid Blue 25
C.I. 62105 C.I. Acid Blue 78
C.I. 67300 C.I. Vat Yellow 2
C.I. 69005 C.I. Vat Black 27
C.I. 70800 C.I. Vat Brown 1

Although more than 20 metric tons of these dyes and pigments may be produced commercially, production data are unavailable; therefore these pigments and dyes are not discussed along with the major dyes listed in Table 2 in the discussions that follow. It is not possible to know exactly what percentage of total U.S. anthraquinone dye production the 18 dyes listed in Table 2 represent, but it is believed to be substantial, probably ranging from 35% to 50%. This report focuses on these 18 dyes and pigments in the discussion of process chemistry and waste production.

Table 2

ANTHRAQUININE DYES AND PIGMENTS OF KNOWN
1978 U.S. COMMERCIAL PRODUCTION
(GREATER THAN 20 METRIC TONS PER YEAR)

C.I. No.	C.I. Name	1978 U.S. Commercial Production (metric tons/yr)	Concentration of the Dye in the Commercial Product (wt%)
69525	Vat Black 25	1036	12.5
60756	Disperse Red 60	656	
61505	Disperse Blue 3	630	
69825	Vat Blue 6	495	8.33
62125	Acid Blue 40	408	
69500	Vat Green 3	393	10
59705	Vat Orange 2	335	12
-	Disperse Blue 64	294	
-	Disperse Red 55	254	
62175	Disperse Red 86	150	
69015	Vat Brown 3	108	11
69025	Vat Orange 15	80	10
58055	Pigment Violet 5:1	46	toner[a]
60755	Disperse Red 4	35	
58000	Pigment Red 83	33	lake[b]
-	Disperse Red 59	29	
61100	Disperse Violet 1	23	
60724	Disperse Violet 27	23	

[a] A toner is an organic pigment that does not contain inorganic pigment, precipitant, or an adsorptive inorganic substrate.

[b] A lake is an organic pigment produced by the interaction of an oil-soluble organic dye, a precipitant, and an absorptive inorganic substrate.

SECTION 2

SUMMARY AND CONCLUSIONS

In this preliminary study of anthraquinone dyes and pigments, 18 dyes and pigments were identified that constitute the major volume of the U.S. 1978 commercial production. Their total production volume was reported to be 5030 metric tons in 1978.

Several solid waste streams were identified that might contain hazardous materials. These include:

- Filter cake from clarifying operations. This cake could contain dye, unreacted intermediates, solvent, by-products formed in the synthesis of intermediates, metallic catalysts, and other impurities.
- Still bottoms from the recovery operations of many of the organic solvents--chlorobenzene, o-dichlorobenzene, acetone, xylene, nitrobenzene, isobutyl alcohol, naphthalene, phenol, and pyridine.
- Discarded shipping containers. These containers, e.g., paper bags and fiber drums used to transport dye and pigment intermediates, and could contain a residual amount of intermediate when emptied.
- Wastewater treatment solids. The evidence suggests that the solids will be contaminated with low levels of all of the dye and pigment intermediates as well as the dye and pigments themselves and some reaction by-products.
- Baghouse fines. The fines are generated during the drying, sizing, standardizing, and packaging of the dyes and pigments. The fines will be principally the dyes and pigments and inert salts.

At any given plant, the major source of discharges of organic chemicals is probably the process wastewater rather than the solid residue stream since, at many locations, the process wastewater includes the mother liquor that contains unreacted intermediates and by-products in potentially high concentrations. Actual emissions will, however, be quite site-specific because emissions will be affected by the disposition of the mother liquor, specific treatment of individual process step wastewaters, the overall wastewater treatment system, the treatment of the filter cakes, and the treatment of still bottoms from the solvent recovery operations.

Identified organic intermediates and other materials of production for the anthraquinone dyes and pigments are listed in Section 4 (Tables 3 and 4). These include the substances that are listed in Section 5 (Table 6) that were identified by the EPA as hazardous wastes.

The information on the producers of dyes and pigments was analyzed to choose a few representative production facilities where a sampling program might be conducted to determine the composition of the waste emissions. The following companies are recommended:

Toms River Chemical Corp.
American Color & Chemical Corp.
American Cyanamid Co.
BASF Wyandotte Corp.
Eastman Kodak Co., Tennessee Eastman Div.
Mobay Chemical Corp., Verona Dyestuffs Div.
Crompton & Knowles Corp., Dyes & Chemical Div., Lowell, NC*

The seven companies that are recommended for a sampling program should yield samples from facilities using different manufacturing and waste treatment practices. Because there is considerable overlap in the actual dyes or pigments that they make, the seven-company sampling program increases the chances of identifying material in the waste streams that may be sensitive to plant practices.

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*Crompton and Knowles Corp. has three facilities that manufacture dyes and pigments. This facility is recommended for sampling because it manufactures exclusively anthraquinone dyes and pigments.

SECTION 3

PROCESS CHEMISTRY

INTRODUCTION

A discussion of the production of Anthraquinone dyes and pigments is necessary to identify the emission sources and wastes that might be hazardous. This section focuses on the chemistry of the dye and pigment synthesis, with special attention given to the starting materials, intermediates, reaction conditions, and potential by-products.

The first anthraquinone vat dye was discovered by Rene Bohn in 1901. This dye, Indanthrone Blue (C.I. Vat Blue 6, C.I. 69825), and the ones that followed had far greater fastness than previous dyestuffs. Anthraquinone acid colors, many prepared from vat dyes by sulfonation, developed rapidly in the years 1893-1907. These dyes had a tremendous impact on the wool-dyeing industry because, unlike previous dyes, they could be applied in a single bath without mordanting.

The introduction of disperse dyes in 1924 by Baddiley, Shepardson, and Ellis coincided with the development of cellulose acetate. These fibers presented a challenge to the dye industry because they absorb less water than natural fibers and are therefore less permeable to polar dyes. Disperse dyes are insoluble in water and are directly applied as fine particles that diffuse into the hydrophobic fibers. The rapid growth of the synthetic fiber industry has made this group of dyes increasingly important.

The anthraquinone dye chemistry uses many synthesis methods; the discussion in this report is, therefore, by no means exhaustive. However, the synthesis of the major dyes and pigments listed in Table 2 are discussed, whenever possible. Anthraquinone dye and pigment manufacturing often deals with processes involving several anthraquinone intermediates. The original anthraquinone dye and pigment production operations were set up to manufacture all intermediates. Because some of these intermediates are produced using hazardous substances, such as mercury catalysts, an industry contact* indicated that many manufacturers now import these basic intermediates, such as the anthraquinonesulfonic acid or 1-aminoanthraquinone, rather than deal with the difficulties involved with the processing and disposal of catalysts.

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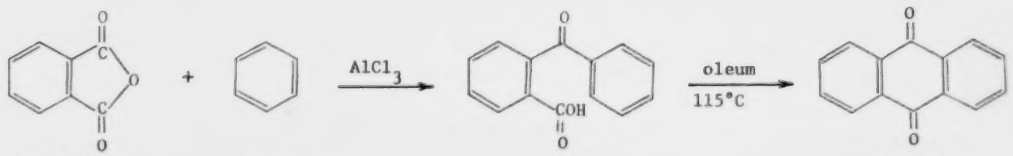
*A. Stein, E. I. DuPont de Nemours & Co., Inc. Dec. 1981. Personal communication.

Whether or not an intermediate is manufactured on-site or purchased will depend on the specific manufacturer and location of the facility. However, because intermediates may be manufactured at some sites, the chemistry of intermediate synthesis is discussed before the actual dye and pigment syntheses is discussed.

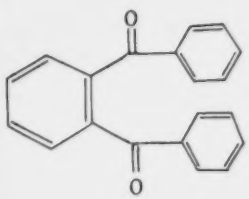
SYNTHESIS OF THE ANTHRAQUINONE RING

The Friedel-Crafts reaction is most commonly used to produce anthraquinone (Morrison and Boyd, 1967). Phthalic anhydride is reacted with benzene in the presence of aluminum chloride yielding o-benzoylbenzoic acid. Ring-closure of this intermediate, or of its substituted derivatives, with concentrated sulfuric acid or oleum (a solution of sulfur trioxide in sulfuric acid) gives the corresponding anthraquinone:



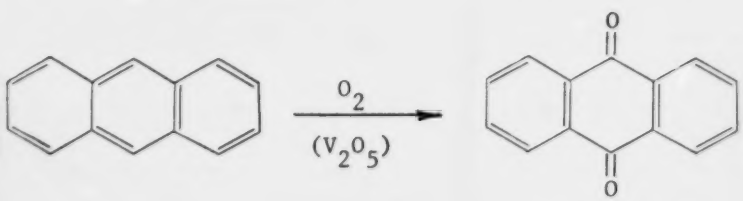
Phthalic Anhydride | Benzene | o-Benzoylbenzoic Acid | Anthraquinone

Diaryl phthalides are often formed as by-products in the o-benzoylbenzoic acid synthesis. The use of tetrachloroethane as a solvent helps to prevent this difficulty, which is particularly evident in phenol condensations (Stilmar and Perkins, 1955).



Diaryl Phthalide

Anthraquinone is also commercially produced by the air oxidation of anthracene using vanadium pentoxide as catalyst (Abrahart, 1968):



Anthracene | Anthraquinone

PREPARATION OF SUBSTITUTED ANTHRAQUINONES

Preparation of Haloanthraquinones

The direct chlorination of anthraquinone in oleum cannot be controlled to yield a monochloro product, but 1,4,5,8-tetrachloroanthraquinone can be prepared by this route. A technically important method of chlorination is the replacement of either an alpha- or a beta-sulfo group by nascent chlorine (from a boiling mixture of potassium chlorate and hydrochloric acid). Many substituted anthraquinones, such as alkyl, hydroxy, and amino derivatives, are readily chlorinated by using relatively mild reagents such as sulfuryl chloride, SO_2Cl_2.

Bromoanthraquinones often result in good yields from the action of free bromine or nascent bromine on the properly substituted anthraquinone. A molecular mixture of sulfuryl chloride and bromine often yields the pure bromo derivative with evolution of hydrochloric acid. Other oxidizing agents, such as sodium hypochlorite or sodium chlorate, can be used in aqueous brominations, permitting full utilization of the bromine (Stilmar and Perkins, 1955).

Preparation of Nitroanthraquinones

Treatment of anthraquinone with nitric acid in 85% sulfuric acid preferentially nitrates the 1-position. The resulting 1-nitroanthraquinone precipitates out of the reaction medium and is not further attacked. Dinitration of anthraquinone with nitric acid in 100% sulfuric acid at 80 to 100°C yields the mixed 1,5- and 1,8-isomers and other less well-defined products. The 1,5-isomer is then separated by crystallization from the sulfuric acid reaction mixture or a solvent (Stilmar and Perkins, 1955).

Preparation of Anthraquinonesulfonic Acids

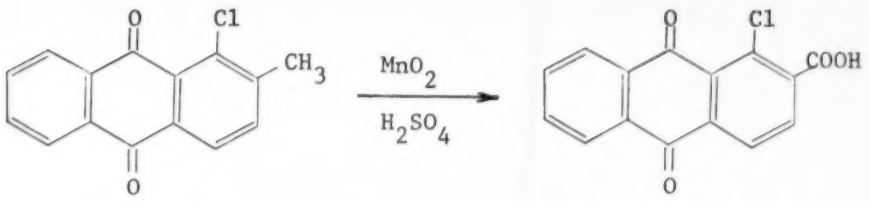
Anthraquinone yields the 2-sulfonic acid with 22% oleum at 145°C. Stronger oleum (48%) at 150°C yields the 2,6- and 2,7-disulfonic acids. The 2,6-isomer may be crystallized out by gradually diluting the sulfonation mass, or it may be salted out in aqueous solution from the more soluble 2,7-isomer by adding sodium sulfate. The presence of one sulfonic acid group prevents any further sulfonation in the same ring. A mercury catalyst in the oleum (20% oleum, 120°C) directs the sulfonic acid into the 1-position instead of the 2-position. Stronger oleum (36%) with a mercury catalyst at 125°C yields 1,5- and 1,8-disulfonic acids. The 1,5-isomer is salted out with a neutral salt from the more soluble 1,8-isomer after dilution (Stilmar and Perkins, 1955).

Preparation of Alkylanthraquinones

The technically important 2-methylanthraquinone is prepared from toluene and phthalic anhydride via the o-(p-toluyl)benzoic acid (Stilmar and Perkins, 1955).

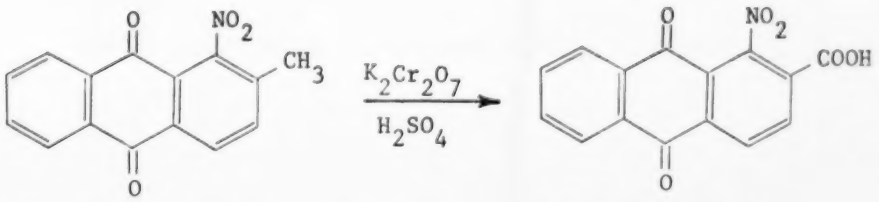
Preparation of Anthraquinonecarboxylic Acids

Anthraquinonecarboxylic acids may be prepared from the nitriles by oxidation. The nitriles can be made by heating haloanthraquinones in nitrobenzene with a cuprous cyanide-pyridine addition compound (Stilmar and Perkins, 1955). The nitriles also can be made by diazotizing the aminoanthraquinone and reacting it with cuprous cyanide. The following two oxidation reactions are of industrial importance as routes to anthraquinonecarboxylic acids:



1-Chloro-2-methyl-anthraquinone

1-Chloro-2-carboxy-anthraquinone

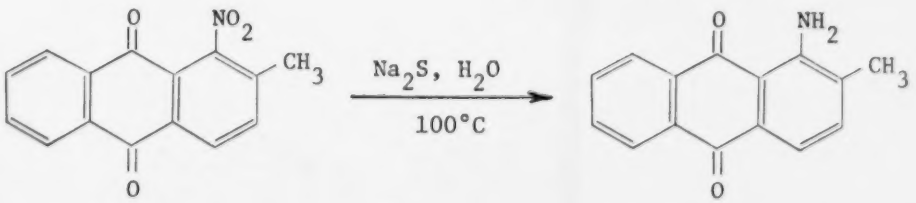


2-Methyl-1-nitro-anthraquinone

2-Carboxy-1-nitro-anthraquinone

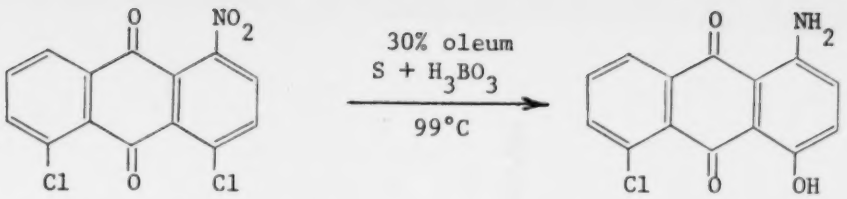
Preparation of Aminoanthraquinones

Aminoanthraquinones result from the reduction of the nitro compounds:



2-Methyl-1-nitro-anthraquinone

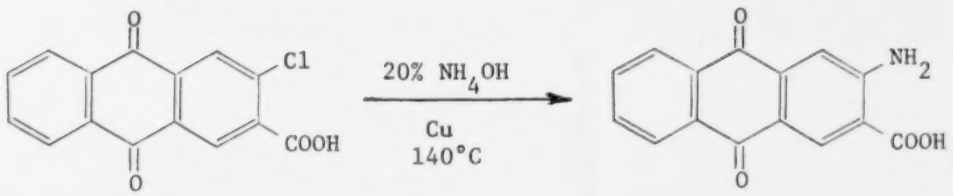
2-Methyl-1-amino-anthraquinone



4,5-Dichloro-1-nitro anthraquinone

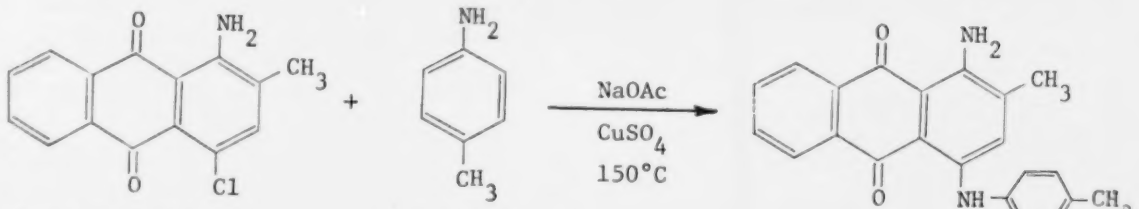
1-Amino-5-chloro-4-hydroxy-anthraquinone

Even more important than the reduction reactions are the replacement reactions applied to halo-, nitro-, or sulfo-substituted anthraquinones (Stilmar and Perkins, 1955). A few are shown below:



3-Carboxy-2-chloro-anthraquinone

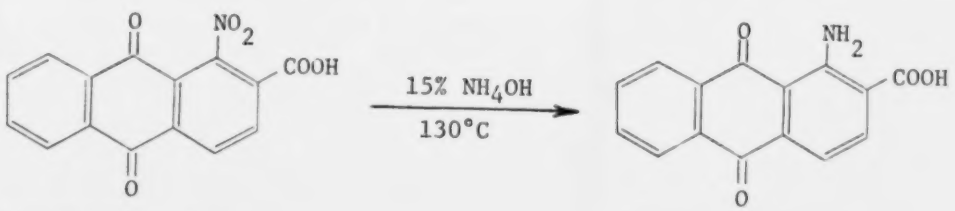
2-Amino-3-carboxy-anthraquinone



1-Amino-4-chloro-2-methylanthraquinone

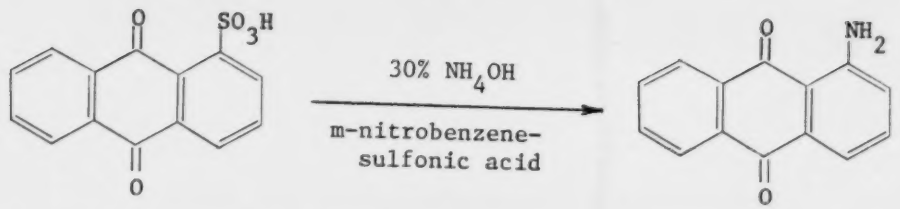
p-Toluidine

1-Amino-2-methyl-4-toluidinoanthraquinone



2-Carboxy-1-nitro-anthraquinone

1-Amino-2-carboxy-anthraquinone

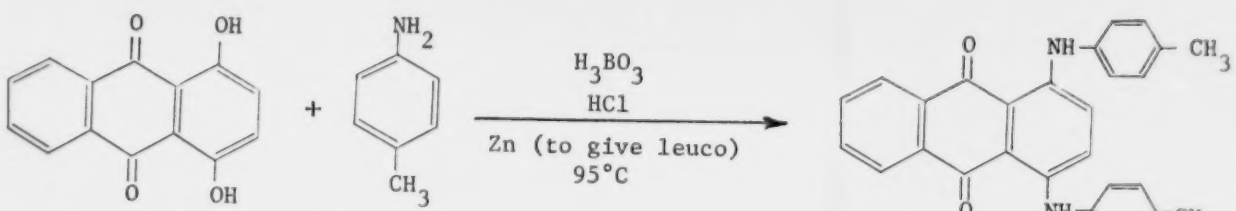


1-Anthraquinonesulfonic Acid

1-Aminoanthraquinone

These aminations require autogeneous pressures often as high as 700 psi (Stilmar and Perkins, 1955).

As a special case, many 1,4-dihydroxyanthraquinones can be aminated to 1,4-diaminoanthraquinones via the leuco derivatives. (These "leuco" forms and this process are discussed later in more detail in the section "Anthraquinone Disperse Dyes.") However, amines can be obtained by the direct amino replacement of the hydroxy in certain hydroxyanthraquinones without intermediate leuco formation (Stilmar and Perkins, 1955):



1,4-Dihydroxy-anthraquinone

p-Toluidine

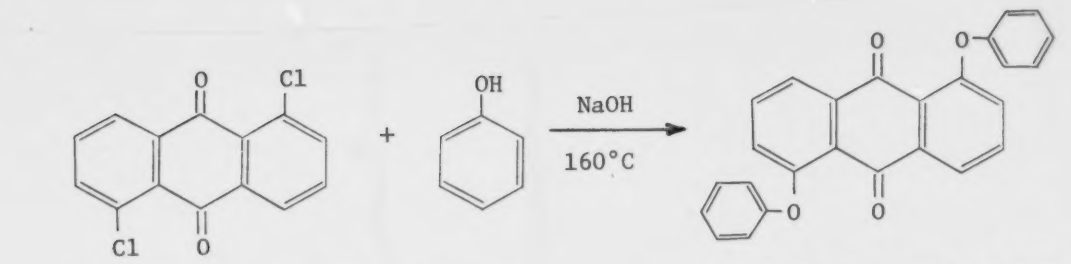
1,4-Di-p-toluidino-anthraquinone

Preparation of Hydroxyanthraquinones

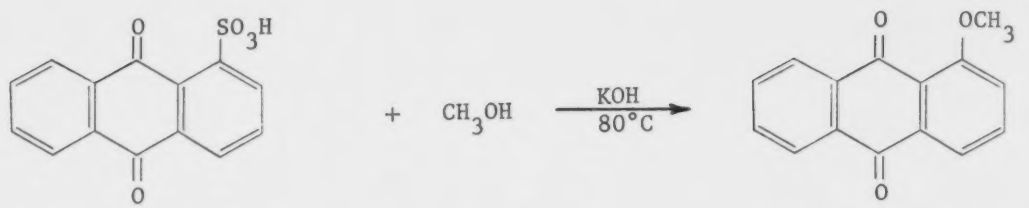
Many anthraquinones may be directly hydroxylated by treatment with oleum, although this procedure usually gives impure products. Quinizarin (1,4-dihydroxyanthraquinone) results from the direct condensation of phthalic anhydride and p-chlorophenol in which sulfuric acid acts as condensing agent, ring-closing agent, and hydrolytic agent for the intermediate chlorohydroxyanthraquinone. Alkaline hydrolysis is also a convenient method for converting most chloro-, nitro-, and sulfoanthraquinones to hydroxy derivatives (Stilmar and Perkins, 1955).

Preparation of Anthraquinone Ethers

Anthraquinone ethers are technically important and may be prepared by displacement of halo or sulfo groups in substituted anthraquinones (Stilmar and Perkins, 1955):



1,5-Dichloroanthraquinone Phenol 1,5-Diphenoxyanthraquinone



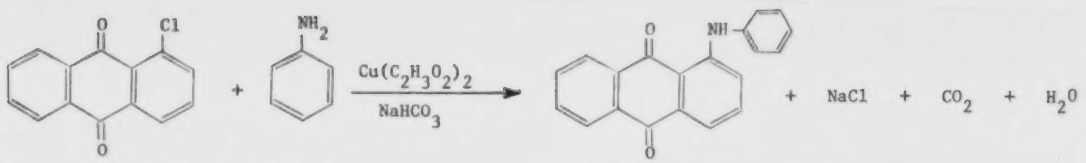
1-Anthraquinonesulfonic Acid Methanol 1-Methoxyanthraquinone

ANTHRAQUINONE ACID DYES

The anthraquinone acid dyes appeared early in the history of anthraquinone dyes in the period from about 1893 to about 1907. Their impact on the wool-dyeing world was tremendous because for the first time there was a class of dyes that could be easily applied like the triphenylmethane, azine, or azo dyes of that period but far exceeded them in light fastness. They had great advantage over the older mordant dyes for wool in their simplicity of application. Unlike the mordant colors, they required no previous preparation of the fiber and were applied in a single bath in a weak acid solution at a temperature near the boiling point.

Anthraquinone acid dyes are, in general, of a lower molecular weight than the anthraquinone vat dyes. Most of them are sulfonic acid derivatives of amino- or aminohydroxyanthraquinone compounds, which may carry one or more of a great variety of substituents. Many of them are prepared by sulfonating the aryl ring of arylamine groups present in the anthraquinone derivatives. Such arylamino compounds, called "bases," usually contain an aniline or p-toluidine group that is easily sulfonated (Buxbaum, 1955). In other cases, the sulfonation takes place in the anthraquinone nucleus itself rather than in any external group.

Acid color bases are generally prepared from haloanthraquinones by means of a reaction worked out by Ullmann. It consists of the condensation of a halogen-containing anthraquinone compound with an organic amine in the presence of a copper catalyst and an acid-binding agent. A simple example is shown below:



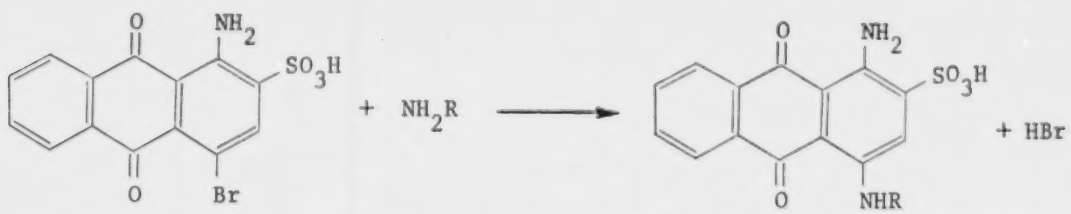
1-Chloroanthraquinone Aniline 1-Anilinoanthraquinone

The reaction is usually conducted in the presence of an unreactive solvent or in the excess of the amine itself acting as solvent. Almost any inert organic solvent may be used; the commonest ones in commercial practice are alcohols, mono- or dichlorobenzene, nitrobenzene, pyridine, or solvent naphtha.

A variety of copper catalysts can be used; the commonest one is basic copper acetate, but the sulfate or chloride may be employed. Sometimes metallic copper can be used advantageously. Sodium carbonate, sodium bicarbonate, or sodium, ammonium, and potassium acetates are usually employed as the acid-binding agent.

The condensation may be either the "dry" type in which conditions are anhydrous and the temperature of reaction is usually from about 130 to 180°C or the "wet" type in which substantial amounts of water are present and in which the condensation is conducted at 100 to 110°C.

To dye wool, the anthraquinone acid color bases must be put into a water-soluble form. Although such solubilizing groups as -COOH, -OH, and -SH have been used as a means of obtaining solution of dyes, the commonest and usually the cheapest method is to introduce one or more sulfonic acid groups. The sulfonations can be accomplished by the replacement of a halogen by a sulfonic acid group, by a sulfonation that employs sulfuric acid or oleum, or by the reaction of an arylamine with bromamine acid (1-amino-4-bromo-2-anthraquinonesulfonic acid):



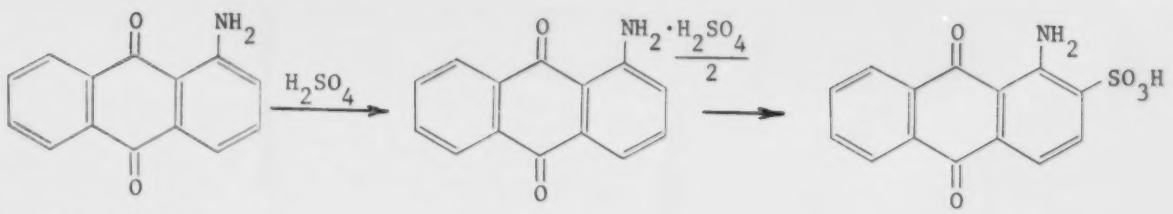
1-Amino-4-bromo-2-anthraquinonesulfonic Acid

Primary Arylamine

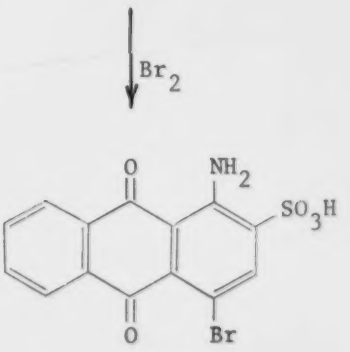
1-Amino-4-"aminoR"-2-anthraquinonesulfonic Acid

In the case of bromamine acid condensations with arylamines, the compounds are isolated directly as the sulfonic acids, and the difficulties involving over- and under-sulfonation that often attend the sulfonation of acid color bases are avoided.

Bromamine acid itself is prepared by sulfonating 1-aminoanthraquinone in the 2 position with sulfuric acid and brominating to bromamine acid:

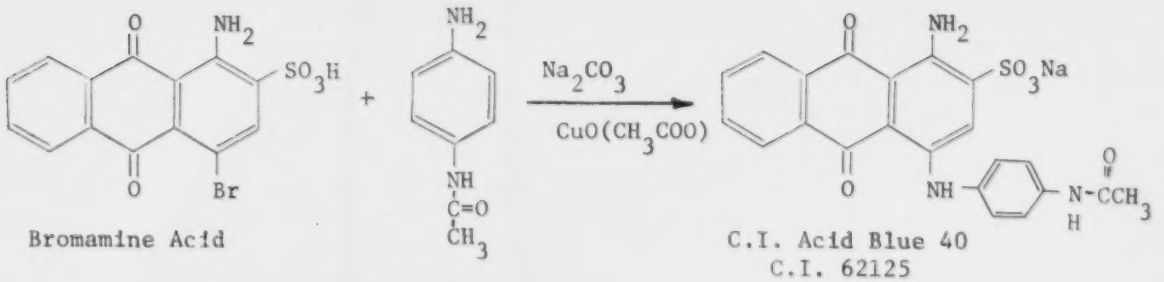


1-Aminoanthraquinone



Bromamine Acid

The dye C.I. Acid Blue 40 (C.I. 62125), the fifth largest volume anthraquinone dye in the United States in 1978 (408 metric tons, Table 2), is produced by the condensation of bromamine acid with p-aminoacetanilide in the presence of copper salts and acid-binding agents, followed by conversion to the sodium salt:



Bromamine Acid

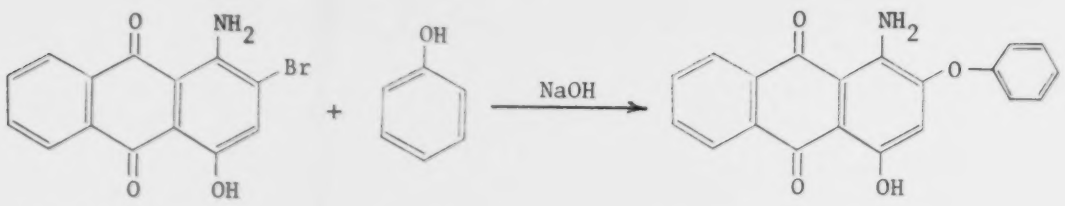
p-Amino-
acetanilide

C.I. Acid Blue 40
C.I. 62125

ANTHRAQUINONE DISPERSE DYES

The anthraquinone disperse dyes were developed for the dyeing of cellulose acetate, nylon, and other hydrophobic fibers. These fibers became commercially important shortly after the end of World War I. Some of these dyes are simple aminoanthraquinones and others are derivatives in which one or more of the hydrogens of the amino group are replaced by alkyl, aryl, hydroxyaryl, hydroxyalkyl, or other groups (Belcher, 1955).

An important method in the preparation of aminoanthraquinones, which was discussed previously, is the replacement reaction applied to halo-, nitro-, or sulfo-substituted anthraquinones. An example of a disperse dye synthesized by replacement of a halogen is C.I. Disperse Red 60 (C.I. 60756), which was the second largest volume anthraquinone dye in the United States in 1978 at 656 metric tons; this dye is formed from 1-amino-2-bromo-4-hydroxyanthraquinone by condensation with phenol in an alkaline medium.

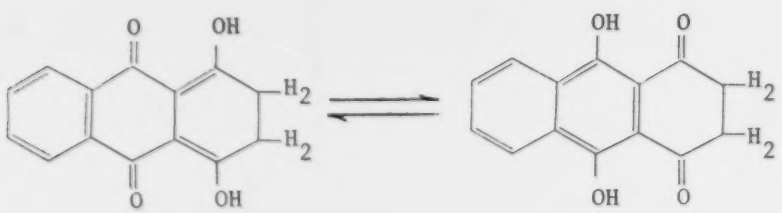


1-Amino-2-Bromo-4-hydroxyanthraquinone

Phenol

C.I. Disperse Red 60
C.I. 60756

An important class of disperse dyes is the 1,4-diaminoanthraquinones (Chung and Farris, 1979). These dyes are usually formed from the amination of 1,4-dihydroxyanthraquinones via the reduced forms called the leuco form (Stilmar and Perkins, 1955). Quinizarin (1,4-dihydroxyanthraquinone), 1-amino-4-hydroxyanthraquinone, and 1,4-diaminoanthraquinone are unique in that they and their related types can form stable leuco derivatives. Leuco-quinizarin may be represented as follows:

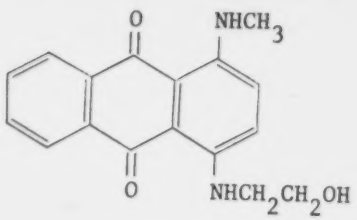


(I) (II)

Infrared measurements seem to support a resonance hybrid of (I) and (II). Some very important technical products are formed by replacing one or both of the hydroxy groups of quinizarin via the leuco form.

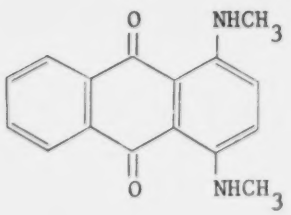
The synthesis of the dye C.I. Disperse Violet 1, C.I. 61100 (1978 U.S. production was 23 metric tons, Table 2) starts with the condensation of quinizarin with aqueous ammonia and sodium hydrosulfite under pressure. The resulting leuco-1,4-diamino-anthraquinone form is then oxidized to the 1,4-diaminoanthraquinone by a mixture of o-dichlorobenzene and nitrobenzene or by nitrobenzene at 150°C with a trace of piperidine.

Another common method for condensation of quinizarin with amines is to use a mixture that is two-thirds quinizarin and one-third leuco-quinizarin. Such a mixture is extremely reactive and in the presence of any one of many organic solvents will react with ammonia, alkylamines, and arylamines. The dye C.I. Disperse Blue 3, C.I. 61505 (the third largest volume anthraquinone dye in the United States in 1978 at 630 metric tons, Table 2), is produced by this method using methylamine and ethanolamine in isobutanol (Stilmar and Perkins, 1955). The alkanol group in this molecule is reported to assist in the dispersion of the dye (Chung and Farris, 1979).



C.I. Disperse Blue 3
C.I. 61505

It should be noted that C.I. Disperse Blue 3 is not just the compound shown. It is a mixture also containing five percent of the following two compounds (BIOS, 1945b):



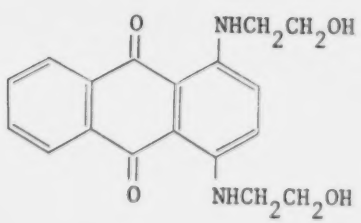
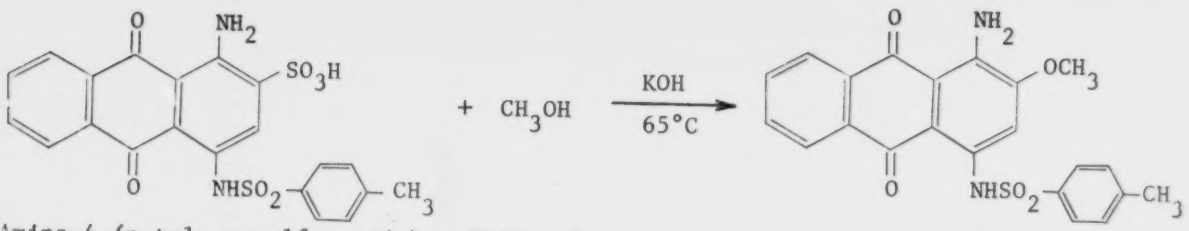


Table 2 lists the anthraquinone dye C.I. Disperse Red 4, C.I. 60755, as being produced at 35 metric tons in the United States in 1978. This dye is formed by the methylation of 1-amino-2,4-dihydroxyanthraquinone (4-amino-xanthopurpurin) with dimethyl sulfate in an acetone-water solution.

The tenth largest volume anthraquinone dye listed in Table 2 (150 metric tons in 1978) is C.I. Disperse Red 86, C.I. 62175. The synthesis of this dye is one example of an anthraquinone ether preparation:



1-Amino-4-(p-toluenesulfonamide)-2-anthraquinonesulfonic Acid

Methanol

C.I. Disperse Red 86
C.I. 62175

ANTHRAQUINONE PIGMENTS and MORDANT DYES

Pigments are substances that impart a positive color to another substance (as opposed to whiting agents, extenders, and fillers). Most pigments are insoluble in organic solvents and water. Numerous instances exist in which the same chemical product serves either as a dye or as a pigment--the distinction between the two types of colorants being based on usage and physical properties rather than on chemical constitution.

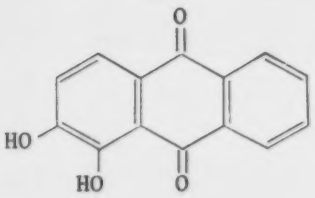
The U.S. International Trade Commission now recognizes three groups of organic pigments: toners, lakes, and reduced toners. Toners are synthetic organic and organometallic pigments sold as full strength colors without diluents. Lakes and reduced toners are extended colors, having been extended by the addition of a solid diluent.

A mordant dye is a dye requiring the use of a mordant to be effective. The mordant is a substance that binds the dye to the textile fiber by forming an insoluble lake in the fiber, the color depending on the metal of the mordant.

Many soluble hydroxyanthraquinones give metallic derivatives that are insoluble and make useful pigments. In these insolubilizations, which are accompanied by color change, alumina hydrate is typically the chief inorganic reactant. It is suggested that both salt formation and chelation take place in the metallizations (Allen, 1955).

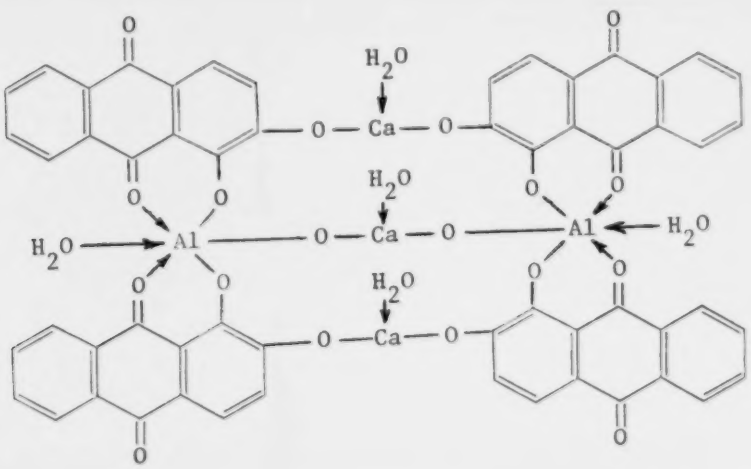
The alizarin type anthraquinone mordant colors require a mordant to develop their shade and characteristic fastness properties. In many cases a two-step operation is used, the mordant first being applied to the cotton or wool fabric, then the dye. In other dyeing methods involving mordant dyes containing solubilizing sulfonic acid groups, the shade of the unmetallized dye is of no interest and the dye must be insolubilized by the addition of some metallic salts to obtain the shade desired.

Alizarin, 1,2-dihydroxyanthraquinone, C.I. Pigment Red 83 or C.I. Mordant Red 11, C.I. 58000, is the oldest and best known pigmentary material of the anthraquinone derivatives.



Alizarin is produced commercially by heating the sodium salt of 2-anthraquinonesulfonic acid with aqueous sodium carbonate and sodium nitrate (or chlorate) in an autoclave at 200°C. However, the synthetic material obtained contains not only alizarin (1,2-dihydroxyanthraquinone) but also flavopurpurin and anthrapurpurin (1,2,6- and 1,2,7-trihydroxy-anthraquinone, respectively) as a result of anthraquinonedisulfonic acid contamination of the 2-anthraquinonesulfonic acid (Chung and Farris, 1979).

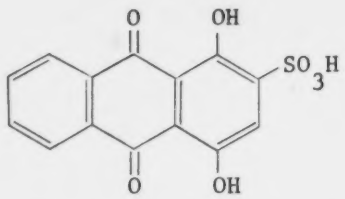
The mordant (premetallized) is depicted as a macromolecule of four alizarin molecules, bonded to two aluminum and three calcium atoms.



In accordance with the assumption that both salt-like and chelate unions are formed, the calcium is the cation in this remarkably stable complex compound, and the chelate union of the two moles of alizarin with one of aluminum constitutes a complex anion (Allen, 1955).

Several metallized amino, sulfo, and carboxy derivatives of the hydroxyanthraquinones have been used as pigments. In these cases, metallization with alumina takes place with greater ease than in the case of

the unmodified hydroxyanthraquinones. Those from the quinizarin derivatives, the Helio Fast Rubines, are used to adjust the shade of other organic pigments. The 4BL shade is the one most widely used--C.I. Pigment Violet 5:1 (aluminum salt), C.I. 58055, with a 1978 U.S. commercial production of 46 metric tons (Table 2).



C.I. Pigment Violet 5:1 (aluminum salt)
C.I. 58055

Chelate ring formation with aluminum probably takes place in the same way as that in the case of alizarin.

ANTHRAQUINONE VAT DYES

Vat dyes are organic coloring matters (with the exception of basic or sulfur colors) that are capable of undergoing a reversible reduction-oxidation cycle without serious color loss or change of shade (Perkins, 1955). No general formula can be written for a vat dye. It is almost always a colored organic compound containing two or more keto groups ($\geqslant C = O$) that are capable of being reduced by sodium hydrosulfite and alkali to give a leuco compound ($\geqslant C-ONa$) that has an affinity for cellulosic fiber. In many cases the affinity extends also to other fibers such as wool, nylon, Orlon, acrylic fiber, and even to cellulose acetate.

In the following paragraphs we discuss the classes of vat dyes represented by the dyes and pigments listed in Table 2.

Pyranthrones

Pyranthrone (8,16-pyranthrenedione) which is representative of one class of vat dyes is manufactured by the synthesis route shown in Figure 1. It has been customary to halogenate pyranthrone to obtain better soaping fastness. The most important halogenated pyranthrone is the dibromo compound, C.I. Vat Orange 2, C.I. 59705:

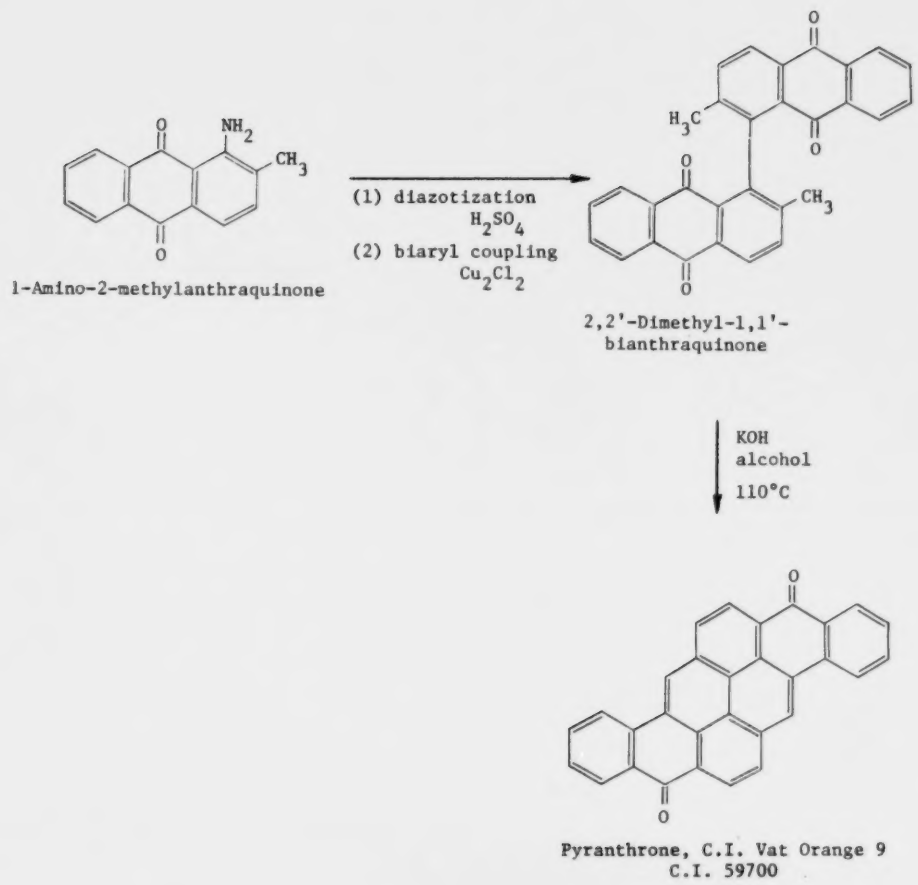
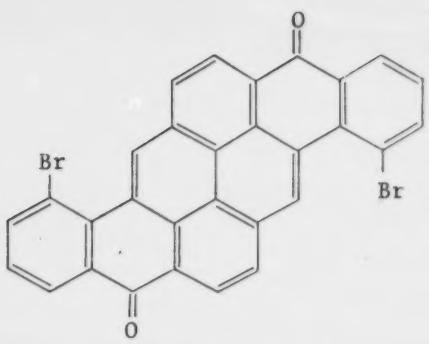


Figure 1 Synthesis of Pyranthrone

Source: Abrahart (1968)

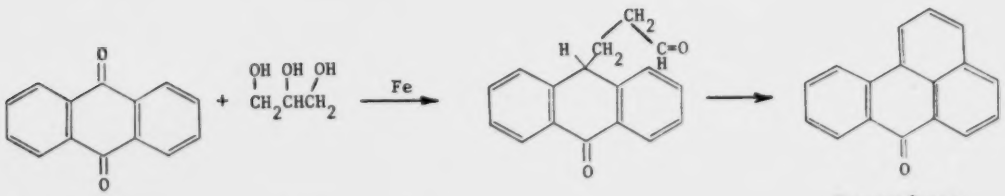


C.I. Vat Orange 2
C.I. 59705

This is prepared by the action of bromine on pyranthrone in chlorosulfonic acid at 60°C with iodine as a catalyst. Many references on anthraquinone dyes state that the position of the bromine atoms is unknown. However, Abrahart (1968) reports that the two bromine atoms are in the 4- and 12- positions.

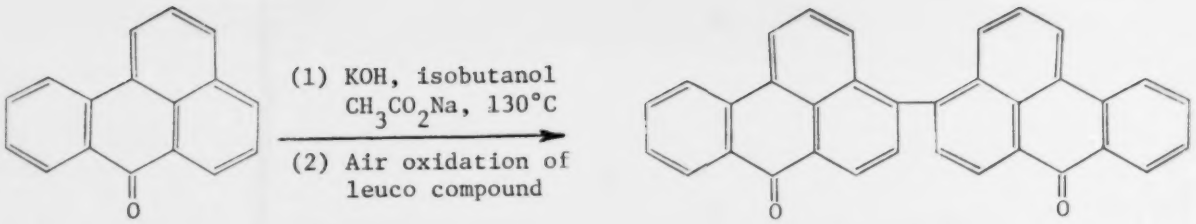
Dibenzanthrones (Violanthrones)

Dibenzanthrone, discovered in 1904, is among the oldest of the anthraquinone vat dyes. The method first used for its preparation is still important commercially and consists of a multiple step synthesis that results in the fusion of two molecules of benzanthrone (7H-benz[de]anthracen-7-one) through a common benzene ring. The benzanthrone required is manufactured by adding a mixture of glycerol and iron borings to anthraquinone in 80 to 85% sulfuric acid at 130 to 140°C:



Anthraquinone Glycerol Benzanthrone

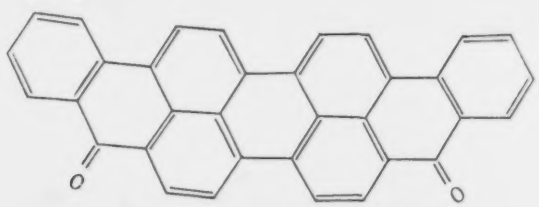
Benzanthrone is then converted into 4,4'-bibenzanthrone (4,4'-dibenzanthronyl) in the following manner (Abrahart, 1968):



Benzanthrone

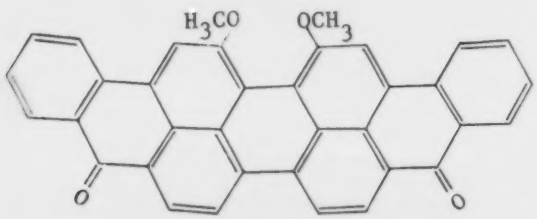
4,4'-Bibenzanthrone

When the 4,4'-bibenzanthrone is treated with manganese dioxide in sulfuric acid at 20°C, the common benzene ring is formed to yield the dibenzanthrone, Violanthrone (C.I. Vat Blue 20, C.I. 59800):



Violanthrone

A very important class of dibenzanthrone derivatives is constituted by the alkyl or alkylene ethers of dihydroxydibenzanthrone. When 4,4'-bibenzanthrone is treated with sulfuric acid and manganese dioxide at 35°C instead of the 20°C used to synthesize Violanthrone, keto groups form at carbon atoms 16 and 17. These keto groups can be reduced to hydroxyl groups by means of 35% aqueous sodium bisulfite. These dihydroxydibenzanthrones are extremely insoluble materials that, after further reduction to the leuco form, dye cotton from deeply colored vats, but the dyes change shade in dilute acids or dilute alkalies, and thus are not practical for general use. The hydroxy compounds can, however, be alkylated under suitable conditions to obtain dyes that are entirely fast to dilute acids and alkalies, and these compounds are extremely valuable because of brilliance of shade, high tinctoral power, and excellent all-around fastness. An important example is C.I. Vat Green 1, C.I. 59825:



C.I. Vat Green 1

Methylation is conducted in trichlorobenzene using methyl p-toluene-sulfonate (Abrahart, 1968) and potassium carbonate at 210°C.

Anthraquinonecarbazoles

Anthrimides are no longer important as vat dyes, but they are necessary intermediates in the preparation of the anthraquinonecarbazoles, a class of dyes characterized by excellent fastness properties and a wide range of shades. The term anthrimide, or dianthrimide (iminodianthraquinone), is used to mean R-NH-R' where R and R' represent the anthraquinone nuclei, and R may or may not be the same as R'.

Anthrimides are produced by the condensation of a haloanthraquinone with an aminoanthraquinone. The reaction is carried out by heating them together in a high-boiling, inert, organic solvent (usually nitrobenzene or naphthalene) in the presence of an acid-binding agent (such as sodium carbonate or sodium acetate) and a copper salt as a catalyst (usually copper acetate). This reaction is generally referred to as the "anthrimide condensation."

The conversion of an anthrimide to an anthraquinonecarbazole, whereby a carbazole ring is formed between two anthraquinone nuclei, is brought about by one of two methods:

(1) Treatment with concentrated sulfuric acid

(2) Fusion with aluminum chloride:

  (a) Dry fusion with aluminum chloride or sodium chloride/aluminum chloride melts.

  (b) Fusion with aluminum chloride complexes of nitrogen-containing compounds, acid chlorides,or nitriles.

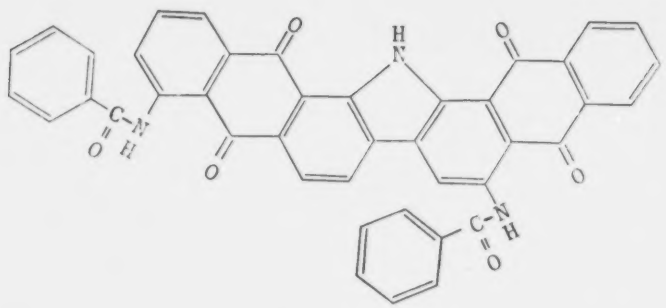
Ring-Closure With Concentrated Sulfuric Acid

The ring-closure method with sulfuric acid is applicable to all anthrimides containing at least two benzamido groups, one in each of the anthraquinone nuclei in the 4-or 5-position. The method employed is simply to dissolve the anthrimide in concentrated sulfuric acid at a temperature below 15°C (to prevent hydrolysis of the benzamido groups). After the mixture is stirred for several hours below 25°C, the ring-closure is complete. The addition of a small amount of ferrous chloride or copper catalyzes the reaction.

Carbazolation produces the product in a reduced form, and it is necessary to subject it to an oxidation procedure. This is customarily conducted with sodium dichromate and sulfuric acid on the dye in a finely divided form suitable for applications. This treatment oxidizes the reduced form of the dye and at the same time destroys impurities present and produces maximum strength and brightness of shade in the residual dye.

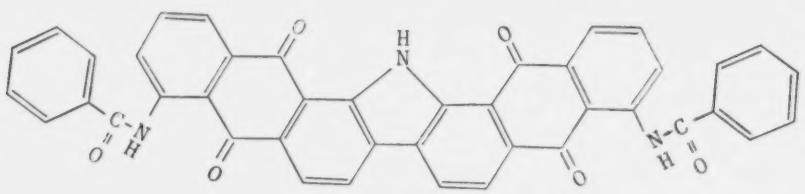
Two of the dyes listed in Table 2 are prepared by this method: C.I. Vat Brown 3 (C.I. 69015) and C.I. Vat Orange 15 (C.I. 69025), which had 1978 U.S. commercial production volumes of 108 and 80 metric tons, respectively.

C.I. Vat Brown 3 is prepared by the condensation of 1-amino-4-benzamidoanthraquinone and 1-benzamido-5-chloroanthraquinone in nitrobenzene along with copper and sodium acetate at 210°C. Nitrobenzene is distilled from the reaction mixture. The residue is then boiled with dilute hydrochloric acid and filtered, yielding 5'-1,1'-dianthrimide. This anthrimide is ring-closed in sulfuric acid and oleum, sodium sulfate, and sodium dichromate:



C.I. Vat Brown 3
C.I. 69015

If the condensation starts with 1-amino-5-benzamidoanthraquinone and the 1-benzamido-5-chloroanthraquinone, 5,5'-1,1'-dianthramide results and this product is ring-closed to yield:

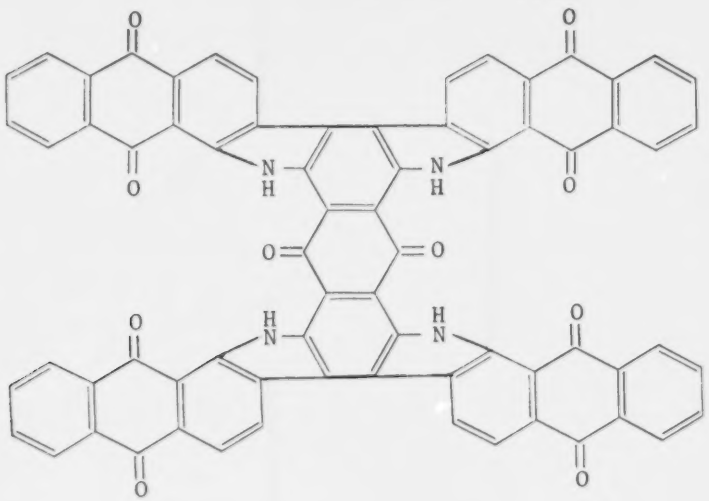


C.I. Vat Orange 15
C.I. 69025

Ring-closure by Fusion

Ring-closure by fusion in aluminum chloride is particularly applicable to the ring-closure of unsubstituted anthrimides. The procedure consists of the fusion of the anthrimide in an anhydrous aluminum chloride/sodium chloride melt at an elevated temperature, often in the presence of an oxidizing agent.

A modification of the procedure is commonly used to carbazolate anthrimides that will not ring-close in sulfuric acid, but that contain benzamido groups. This procedure involves forming a complex of aluminum chloride with nitrogen-containing solvents (such as nitrobenzene) or with tertiary amines (such as pyridine), or by the addition of acid halides or organic nitriles. C.I. Vat Green 8 (C.I. 71050) is formed using this alternative method. 1-Aminoanthraquinone and 1,4,5,8-tetrachloroanthraquinone are condensed in the presence of copper and nitrobenzene to form a pentanthrimide that is cyclized with aluminum chloride. This product is again subjected to an oxidative procedure in sodium dichromate and sulfuric acid:



C.I. Vat Green 8
C.I. 71050

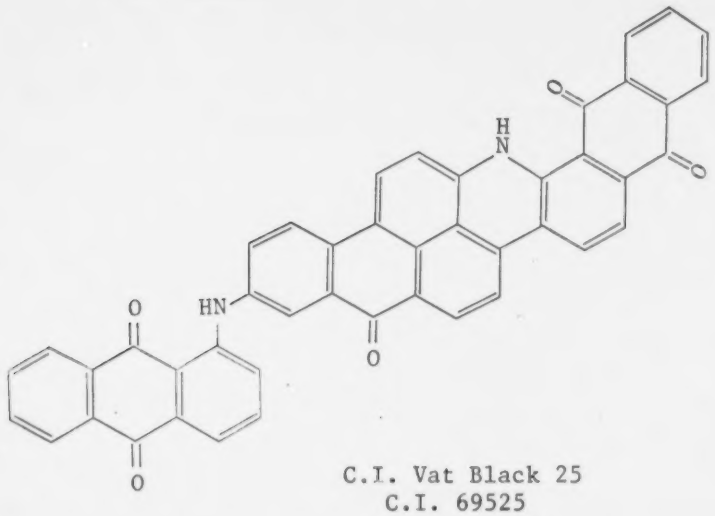
Benzanthroneacridines

The benzanthroneacridine vat dyes are prepared by alcoholic caustic fusion of 3-(1-anthraquinoylamino)benzanthrones at an elevated temperature. The fusion mass is then poured into water where the dye in its reduced form is soluble. The reduced product is oxidized and separated as an insoluble precipitate.

Substituted products can be prepared by using ring-substituted α-aminoanthraquinones instead of 1-aminoanthraquinone, such as 1-amino-5-benzamidoanthraquinone, or an aminoanthraquinone to which a heterocyclic system is attached. 3-(1-Anthraquinoylamino)benzanthrones may be halogenated and the halogenated product condensed with α-aminoanthraquinones. These, on fusion, produce a series of dyes varying in shade from olive to brown (Perkins, 1955).

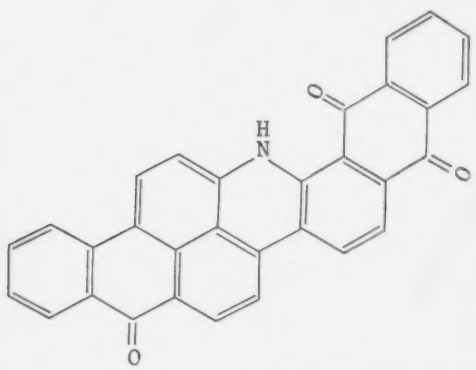
Two very important anthraquinone vat dyes are in the benzanthroneacridine class. Table 2 lists C.I. Vat Black 25, C.I. 69525, as first and C.I. Vat Green 3, C.I. 69500 as sixth in 1978 U.S. commercial production volume with quantities of 1036 and 393 metric tons, respectively.

C.I. Vat Black 25 is produced by the condensation of 2 moles of 1-aminoanthraquinone with 1 mole of 3,9-dibromobenzanthrone in boiling naphthalene with copper oxide and sodium carbonate at 210 to 220°C. The intermediate anthrimide is cyclized with potassium hydroxide in boiling isobutyl alcohol to form the dye:



C.I. Vat Black 25
C.I. 69525

If 1 mole of 1-aminoanthraquinone and 1 mole of 3-bromobenzanthrone are used during condensation, then C.I. Vat Green 3 results:

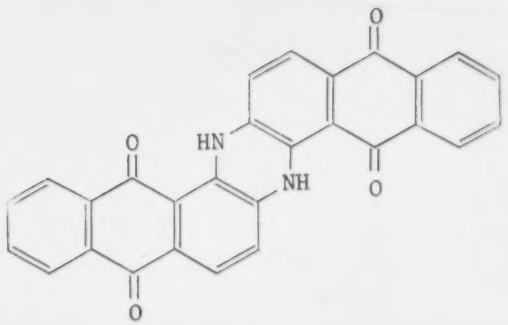


C.I. Vat Green 3
C.I. 69500

Anthraquinoneazines

The anthraquinoneazines are an important class of vat dyes, with two main types: 1,4-diazines (represented by indanthrone), which are used in large volume, and the s-triazines (cyanuric acid derivatives), which are used to a lesser degree.

Indanthrone, 6,15-dihydro-5,9,14,18-anthrazinetetrone and its derivatives are the most important dyes of the 1,4-diazine class. Discovered in 1901, indanthrone (C.I. Vat Blue 4, C.I. 69800) was the first vat dye of the anthraquinone series. Indanthrone is the source of the principal blue vat dyes.



C.I. Vat Blue 4
C.I. 69800

Indanthrone is produced commercially by the fusion of 2-aminoanthraquinone, usually with a mixture of sodium and potassium hydroxides and an oxidizing agent such as sodium nitrate at about 215 to 220°C. The impure product, obtained in the reduced leuco form, may be purified by allowing the leuco sodium salt of the indanthrone to crystallize from the vat of the crude dye, which is then filtered. The leuco form is then oxidized to the dye by air, oxygen, or alkaline oxidizing agents. The yield of pure indanthrone under the most favorable conditions is about 55 percent. The dye at this stage is usually pure enough for most purposes, but further purification can be accomplished by crystallizing it as a sulfate from 85% sulfuric acid.

Indanthrone as a vat dye is now much less important commercially than in former years because of its objectionable sensitivity to bleaching. Chlorinated derivatives are used to overcome this sensitivity to bleaching. Indanthrone is either chlorinated directly or a dichloro derivative is prepared by a synthesis using anthraquinone derivatives. This latter approach is illustrated in the preparation of 7,16-dichloroindanthrone, C.I. Vat Blue 6, C.I. 69825, by condensing 2-amino-1,3-dibromoanthraquinone with itself to produce 7,16-dibromo-indanthrone, followed by the replacement of bromine atoms with chlorine. 7,16-Dichloroindanthrone can also be prepared by the direct condensation of 2-amino-1-bromo-3-chloro (or 1,3-dichloro)anthraquinone with itself. C.I. Vat Blue 6 was the fourth largest commercially produced anthraquinone dye by volume in the United States in 1978 (Table 2) at 495 metric tons.

SECTION 4

DYE INTERMEDIATES

A list of the intermediates used in the United States for manufacture of dyes and pigments based on anthraquinone was compiled from information in the Colour Index (The Society of Dyers and Colourists, 1980). Table 3 lists the organic intermediates and chemical reagents for the large volume anthraquinone dyes and pigments that were listed in Table 2. Table 4 lists the organic intermediates and chemical reagents for the remaining dyes and pigments listed in Table 1. These dyes have unknown commercial production rates or were produced at a rate of less than 20 metric tons per year in 1978. Intermediates used to manufacture dyes and pigments whose ingredients were not published in the Colour Index could not be included in the listings: this included 5 out of the 18 dyes and pigments listed in Table 2 and 66 of the remaining 127 dyes.

Tables 3 and 4 also identify those substances which, if present in solid wastes, are subject to regulation by the EPA as hazardous wastes under RCRA (Federal Register, 1980). These substances are identified by their hazard code.

Table 3

ORGANIC INTERMEDIATES AND CHEMICAL REAGENTS USED TO PRODUCE ANTHRAQUINONE DYES AND PIGMENTS(WITH KNOWN 1978 COMMERCIAL PRODUCTION GREATER THAN 20 METRIC TONS)

Intermediates	Hazardous Waste Listing[a]
Acetanilide, p-amino-	
Anthracene, m-nitro derivatives	
Anthraquinone	
____, 1-amino- (Fast Red Base AL)	
____, 1-amino-5-benzoylamino-	
____, 2-amino-1-bromo-3-chloro-	
____, 1-amino-2-bromo-4-hydroxy-	
____, 2-amino-3-chloro-	
____, 2-amino-1,3-dichloro-	
____, 1-amino-2,4-dihydroxy- (4-Aminoxanthopurpurin)	
____, 1-benzamido-4-chloro-	
____, 2-chloro-	
____, 1-chloro-5-amino-	
____, 1-chloro-4-benzamido-	
____, 1-chloro-5-benzamido-	
____, 1-chloro-5-nitro	
____, 1,5-diamino-	
____, 1,2-dibromo-	
____, 1,4-dihydroxy- (Quinizarin)	
____, 2-methyl-	

[a] Hazard codes from the Federal Register (1980), indicate the basis for EPA listing the material hazardous: Ignitable (I), Corrosive (C), Reactive (R), EP Toxic (E), Acute Hazardous (H), and Toxic (T).

Table 3 (continued)

Intermediates	Hazardous Waste Listing
1-Anthraquinonesulfonic acid, 5-nitro-	
_____, potassium salt	
2-Anthraquinonesulfonic acid (Silver Salt B) (β acid)	
_____, 1-amino-4-bromo- (Bromamine acid)	
Benzanthrone (7H-Benz[de]anthracene-7-one)	
_____, 3-bromo-	
_____, 3,9-dibromo-	
Benzene, chloro-	T
Benzoyl chloride	
Chlorobenzoylbenzoic acid	
Dimethyl sulfate	T
Ethanolamine	
Indanthrone (6,15-Dihydro-5,9,14,18-anthrazinetetrone)	
Leuco-quinizarin	
Methylamine	
Phenol	T
Phthalic anhydride	T
Pyranthrone	

Table 3 (concluded)

Reagents	Hazardous Waste Listing
Acetone	I
Copper acetate, basic	T
o-Dichlorobenzene	T
Isobutyl alcohol	I,T
Naphthalene	T
Nitrobenzene	I,T
Piperidine (Hexahydropyridine)	
Sodium acetate, anhydrous	
Sodium carbonate	

Table 4

ORGANIC INTERMEDIATES AND CHEMICAL REAGENTS USED TO PRODUCE ANTHRAQUINONE DYES AND PIGMENTS

Dyes and Pigments of Unknown U.S. Commercial Production or < 20 Metric Tons in 1978

Intermediate or Reagent	Hazardous Waste Listing[a]
Acetic acid, glacial	
Acetanilide, p-amino-	
_____, p-amino-N-methyl-	
Aniline	I
_____, p-butyl-	
_____, p-chloro-	H,T
_____, p-(2-hydroxyethyl)-	
_____, p-methoxy- (p-Anisidine)	
_____, o-nitro- (Fast Orange GR)	
_____ 2,4,5-trimethyl- (Mesidine)	
Anthanthrone (Dibenzo[cd,jk]pyrene-6-12-dione)	
Anthracene	
_____, 9-hydroxy- (9-Anthrol) (α-Anthrol)	
Anthraquinone, 1-amino- (Fast Red Base AL)	
_____, 2-amino-	
_____, 1-amino-4-anilino-2-bromo-	
_____, 1-amino-4-benzamido-	
_____, 1-amino-2-bromo-	
_____, 1-amino-2-bromo-4-(2-sulfo-p-toluidino)-	

[a]Hazard codes from the Federal Register (1980) indicate the basis for EPA listing the material hazardous: Ignitable (I), Corrosive (C), Reactive (R), EP Toxic (E), Acute Hazardous (H), and Toxic (T).

Table 4 (Continued)

Intermediate or Reagent	Hazardous Waste Listing[a]
Anthraquinone, cont.	
_____, 1-amino-2,4-dibromo-	
_____, 2-amino-3-hydroxy-	
_____, 1-benzamido-4-chloro-	
_____, 2-bromo-1,4-dihydroxy-	
_____, 1-bromo-4-hydroxy-	
_____, 1-bromo-4-methylamino-	
_____, 1-chloro-	
_____, 1-chloro-4-hydroxy-	
_____, 2,6-bis(α-chlorobenzylideneamino)-	
_____, 2-chloro-1,4-dihydroxy-	
_____, 1,4-diamino-	
_____, 2,6-diamino-	
_____, 2,6-diamino-1,5-dichloro-	
_____, 4,8-diamino-1,5-dihydroxy-	
_____, 2,6-diamino-1,5-dimercapto-	
_____, 1,4-diamino-2-hydroxy-	
_____, 2,4-dianilyl-1-hydroxy-	
_____, 2,6-dibenzamido-	
_____, 2,6-dibromo-1,5-dihydroxy-4,8-dinitro-	
_____, 1,4-dichloro-	
_____, 1,5-dichloro-	
_____, 1,8-dichloro-	
_____, 2,6-dichloro-1,5-dihydroxy-4,8-dinitro-	
_____, 5,8-dichloro-1,4-dihydroxy- (5,8-Dichloroquinizarin)	
_____, 1,4-dihydroxy- (Quinizarin)	
_____, 1,5-dihydroxy- (Anthrarufin)	

Table 4 (Continued)

Intermediate or Reagent	Hazardous Waste Listing[a]
Anthraquinone, cont.	
_____, 1,8-dihydroxy-4,5-dinitro-	
_____, N,N-dimesityl-1,4-diamino-	
_____, 1,5-dimethoxy-4,8-dinitro-	
_____, 1,5-dinitro-	
_____, 1,8-dinitro-	
_____, N,N-di-p-toluyl-1,4-diamino-5,8-dihydroxy-	
_____, 1-hydrazino-	
_____, 1-hydroxy-	
_____, 1-hydroxy-4-nitro-	
_____, 1-methoxy-	
_____, 1,4,5,8-tetrachloro-	
_____, 1,2,4-trihydroxy- (Purpurin)	
2-Anthraquinonecarbonyl chloride, 1-nitro-	
2,5-Anthraquinonedisulfonic acid, 1-amino-4-bromo-	
2,6-Anthraquinonedisulfonic acid, 4,8-diamino-1,5-dihydroxy-	
_____, 4,8-dibromo-1,5-dihydroxy-	
_____, 1,5-dihydroxy-4,8-dinitro-	
2,8-Anthraquinonedisulfonic acid, 1-amino-4-bromo-	
1-Anthraquinonesulfonic acid	
_____, 8-hydroxylamino-	
_____, 3-nitro-	
2-Anthraquinonesulfonic acid, 1-amino-4-bromo- (Bromamine acid)	
_____, 1-amino-4-(p-toluenesulfonamide)-	
_____, 1,4-diamino-	
_____, 4,8-diamino-1,5-dihydroxy-	
_____, 1,5-dimethoxy-4,8-dinitro-	
5-Anthraquinenesulfonic acid, 1-amino-2-bromo-4-(p-acetamidoanilino)-	
8-Anthraquinone sulfonic acid, 1-amino-2-bromo-4-(p-acetamidoanilino)-	

Table 4 (Continued)

Intermediate or Reagent	Hazardous Waste Listing[a]
Benzaldehyde	
Benzanthrone (7H-Benz[de]anthracene-7-one)	
_____, 3-benzoyl-	
_____, 3-chloro-	
_____, dichloro- (isomer unspecified)	
_____, 2-methoxy-	
3-Chlorobenzanthrone sulfide	
3-Chlorobenzanthrone selenide	
Benzotrichloride	E
Benzene, chloro-	C,R,T
_____, nitro- (Myrbane oil)	T
_____, trichloro- (isomer unspecified)	I,T
1,1'-Bianthraquinone, bromo-2,2'-dimethyl-	T
_____, 2,2'-dimethyl-	
(1,1'-Binaphthalene), 8,8'-dicarboxylic acid	
4-Biphenylcarboxylic acid, 4'-nitro-	
2,2'-Biphenyldiamine	
Chloroacetic acid	
Cyclohexylamine	
1,1-Dianthrimide, 4,4-dibenzamido-	
Dibenzanthrone (Violanthrone)	
_____, 16,17-dihydroxy-	
4,4'-Dibenzanthronyl	
1,5-Dibenzoylnaphthalene	
1,6-Dibenzoylpyrene	
1,2-Dibromoethane	T

Table 4 (Concluded)

Intermediate or Reagent	Hazardous Waste Listing[a]
Glycerol	
Indanthrone (6,15-Dihydro-5,9,14,18-anthrazinetetrone)	
Indanthronedisulfonic acid	
Kerosene	
Leuco-quinizarin	
Leuco-1,4,5,8-tetrahydroxyanthraquinone	
Methylamine	
1,4,5,8-Naphthalenetetracarboxylic acid	
N-Methylnaphthalimide	
3,4,9,10-Perylenetetracarboxylic diimide	
Phenol	T
o-Phenylenediamine	
_____, 4-ethoxy-	
Potassium acetate	
Potassium anthranilate	
Potassium formate	
Pyranthrone	
Pyridine	T
p-Toluidine (p-Aminotoluene)	
p-Toluenesulfonamide	
p-Toluenesulfonate, 2-chloroethyl-	
Xylene	I,T
Anthra(1,9)pyrazole-6(2H)-one	
___, 3-bromo-	
Arsenic acid	E
Ethanol	
Glucose	

SECTION 5

SOURCES OF WASTE DISCHARGES DURING DYE AND PIGMENT MANUFACTURING

The wide range of dye and pigment production processes and the specific plant characteristics and process control capabilities make estimation of material losses during dye manufacture a difficult task. In general, though, the most significant material losses will be intermediates that do not react and by-products such as incomplete dye or pigment molecules. The intermediates and by-products from the dye manufacture will be present either in the product or in the solid waste streams regulated under RCRA, which include wastewater, solid residuals, and the vapor and dust emissions. The material in the wastewater may be discharged in the plant effluent (although some will be destroyed by treatment), and some will be discharged on wastewater treatment solids. Solvent recovery techniques such as distillation are used in many anthraquinone dye and pigment manufacturing processes. Many of these solvents are defined as hazardous materials by the EPA under RCRA and the still bottoms from their recovery are also considered hazardous waste discharges.

OVERVIEW OF DYE AND PIGMENT PRODUCTION PROCESSES

Figure 2 illustrates the dye and pigment manufacturing process and shows where the losses of materials occur. Dyes or pigments are usually prepared in batch processes; thus the manufacturing plant typically contains several reactor trains. Complex dyes and pigments may require use of several reactor trains. Production of colors is usually rotated by set schedules from light- to dark-colored dyes to minimize the impact of dye carry-over from multiple use of the equipment.

The dye manufacturing equipment required to produce anthraquinone dyes and pigments consists of storage tanks, measuring tanks, reaction kettles, high pressure autoclaves, filter presses, suction filters, pressure filters, oven-type air dryers, and vacuum chamber dryers. A unique piece of equipment is the Venuleth. This versatile vessel can be used as a

- Dryer for aqueous slurries
- Still for recovery of solvents by direct atmospheric distillation
- Agitated steam still
- Reaction vessel.

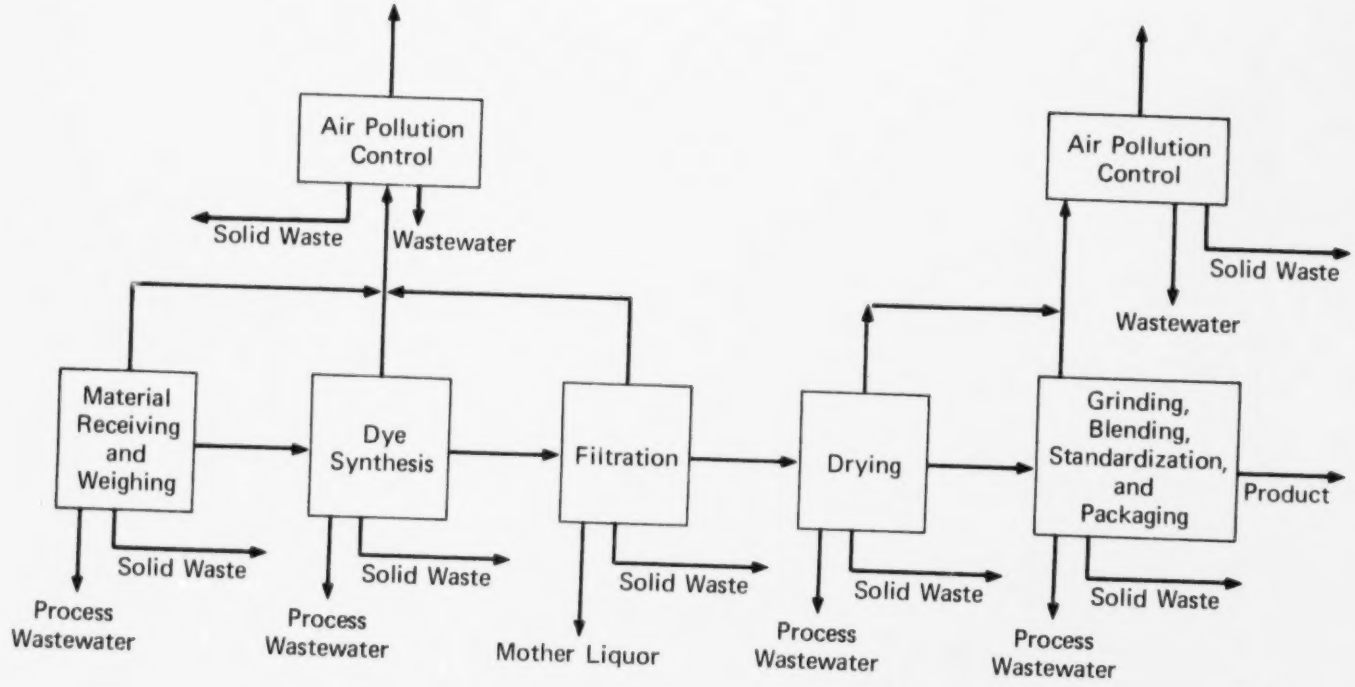


FIGURE 2 PRODUCTION OPERATIONS THAT ARE SOURCES OF WASTE EMISSIONS IN DYE AND PIGMENT MANUFACTURE

They resemble standard, horizontal, agitated, jacketed vacuum dryers, and they are mainly used as rotary vacuum dryers attached to condensers for the recovery of solvents (Bradley and Kronowitt, 1954). Another piece of specialized apparatus is a vacuum sublimer. The sublimers are used for the purification of several intermediates, such as benzanthrone and the aminoanthraquinones, which sublime readily.

Anthraquinone dye and pigments constitute a large and varied class of chemical compounds, as indicated in Section 3. Sometimes the manufacturing process is a single-step condensation reaction; other times the manufacturing entails a series of chemical reactions performed at widely different temperatures and pressures and with varying solvents. The organic reactions are performed at temperatures varying from -18^{o} to $260^{o}C$ and at pressures varying from 29 inches of vacuum to over 600 psi. Equipment flexibility is necessary for such a variety of products and processes. The materials of construction include lead-, glass-, or rubber-covered steel, mild steel, stainless steel, and corrosion-resistant alloys. Storage tanks range in volume from 10,000 to 50,000 liters and reaction vessels from 1,000 to 20,000 liters.

An important aspect of anthraquinone dye and pigment production is the volume of raw materials required to produce the commercial dyestuff. Bradley and Kronowitt (1954) report that 10,000 metric tons of various raw materials were required to produce 1,820 metric tons of various anthraquinone vat dye commercial dyestuffs. Chief among the raw materials were sulfuric acid, caustic soda, hydrochloric acid, phthalic anhydride, ammonia, benzene, nitrobenzene, glycerol, and alcohol. BIOS reports (1945a,b,c) provide detailed information concerning the production of 9 of the 18 major anthraquinone dyes and pigments known to be produced in amounts greater than 20 metric tons per year. An analysis of this information is summarized in Table 5. The average ratio of mass of the raw materials to commercial dyestuff is 4.8:1 (the manufacture of Vat Orange 15 was not included in this average because its production requires the synthesis of more intermediates than is typical of the anthraquinone dyes and pigments); this is comparable to the 5.5:1 reported in Bradley and Kronowitt (1954) for the vat dyes produced at the Toms River, NJ, manufacturing facility.

The majority of the vat dyes produced are sold in paste form in varying concentration, from 6 to 30% dye. The standardization of dye pastes usually consists of conventional paste grinding, with the addition of conditioning agents to regulate the fluidity of the paste. Aryl sulfonic acid derivatives are among the conditioning agents used. Glycerol is added to printing pastes. A small amount of the vat dyes produced are sold as dry powders, and neutral salts are often added to standardize the powders. The amount of salt added to a dye depends on the dye and the producer and may even vary among dye batches at a single facility. The diluent will usually contain wetting agents and emulsifiers and dedusters (usually hydrocarbon oils) to improve the dyestuff properties.

Disperse dyes are also sold in powder form, varying in concentration from 20 to 50% dye, or in paste form at 10 to 25% dye concentration.

Table 5

MATERIAL REQUIREMENTS FOR PRODUCTION OF SOME ANTHRAQUINONE DYES AND PIGMENTS

C.I. Name	C.I. No.	Material Requirements Kg Per 100 Kg of Dye[a]		Concentration of the Dye in the Commercial Product (wt%)	Ratio of Mass of Raw Materials to Commercial Dyestuff
		Inorganic & Organics	Organics		
Vat Black 25	69525	1311	853	12.5	2.5
Disperse Blue 3	61505	954	954	~ 80	7.8
Vat Blue 6	69825	1420	91	8.33	2.1
Vat Green 3	69500	1302	562	10	2.2
Vat Orange 2[b]	59705	1078	80	12	11.7
Vat Brown 3[b]	69015	839	824	11	4.4
Vat Orange 15[b]	69025	75000	8569	10	940
Pigment Violet 5:1	58055	492	68	100	4.9
Pigment Red 83	58000	360	137	~ 80	3.1

[a] The raw materials in this analysis include some of the basic anthraquinone starting materials, such as quinizarin, 1-aminoanthraquinone, and benzanthrone, from which more complex intermediates are synthesized.

[b] The BIOS reports (1945a,b,c) give the material requirements for production of these dyes as paste at standard commercial strength. All of the other dyes were produced at pure strength and later standardized.

Pigments, which are insoluble, are handled slightly differently; 45% of all pigments are dried, ground, and sold without dilution (Lapp et al., 1979). Another 40% are flushed (dispersed into an oil phase), which adds 65% inert ingredients (Steadman et al., 1977). The remaining 15% of all pigments are sold as wet filter press cake without processing.

The mother liquor (remaining after filtering out the intermediates synthesized during dye manufacture or the dye or pigment product) and other process wastewater are treated by sedimentation and activated sludge by some dye manufacturers before discharge. Other dye manufacturers discharge these wastes directly to municipal sewer systems so that treatment occurs at a publicly owned treatment works.

RAW MATERIAL RECEIVING AND HANDLING

Liquid raw materials are often stored in a tank farm consisting of large (~ 50,000 liter) tanks for the materials used in large quantities, such as sulfuric acid, oleum, caustic, aqueous ammonia, hydrochloric acid, and benzene. Other organic solvents are also stored in a solvent tank farm. These materials are pumped directly to storage tanks, to measuring tanks, and finally to the reaction vessels. Dye intermediates are received either from other chemical manufacturing sites or from manufacturing operations at the dye manufacturing site. Material from other manufacturing sites is likely to arrive in fiber drums or paper bags. Material from the same site may arrive the same way or in some container, such as a tote box, designed for transfer and temporary storage of solids. Some dyestuff intermediates filter cakes are transported within a manufacturing facility in carts called "cake cars," which are hitched together and drawn by small tractors (Bradley and Kronowitt, 1954). The intermediates are weighed and transferred into the appropriate vessels in the dye reactor train. Powder loading, unloading, filling, and weighing may be performed under hoods with exhausters and dust-collecting equipment (Boeniger 1980).

Solid Wastes

Most solid wastes from material receiving will be shipping containers contaminated by chemicals that stick to the walls or fill cracks and crevices. Very few data are available to indicate the disposition of this material. One industry contact* stated that his company, which manufactures dyes and pigments based on anthraquinone, sends about one truckload of fiber drums and paper waste to a solid waste disposal site every day. Any chemicals remaining in the drums or on the paper would end up at the dump site. Manufacturing operations that receive material in temporary storage and transportation containers from their own chemical manufacturing operation may wash the containers and return them to duty so any chemicals remaining in the

*Personal communication M. B. Bochner, Atlantic Chemical Company, September 10, 1980.

container would then go into the process wastewater treatment system (see below).

Process Wastewater

The material from spills during transfer operations and residual material in temporary storage and transfer containers may be washed away. The amount of water required and the frequency of cleaning is difficult to quantify, and no quantitative estimates have been made.

Vapor and Dust Losses

Vapor losses during chemical intermediate transferring and weighing operations are expected to be small because most of the chemicals are estimated to have low vapor pressures and be solids at room temperature. The loss of solid material from dusts may occur during handling. The vapors and dusts at the weighing and transfer operations at some facilities will be vented to a scrubber unit (Keinath, 1976; DETO, 1980; Bradley and Kronowitt, 1954).

DYE SYNTHESES

Solid Residuals and Concentrated Liquid Wastes

A solid residual produced during dye synthesis is the discharge from filter presses used during intermediate synthesis operations. These solid residues include material from processing spills during material transfer operations and filter cake from solution clarifications. The expected organic components include intermediates, unreacted raw materials, and unidentified reaction by-products. The amounts produced have not been quantified.

The production of anthraquinone dyes and pigments entails the use of significant amounts of organic solvents. These solvents are recovered from reaction mixtures using Venuleths as described previously. The recovered solvents and the still bottoms resulting from the distillation may represent a significant hazard, as specified in the RCRA identification and listing of hazardous wastes from nonspecific sources. The solvents used in anthraquinone dye and pigment production that are included in this listing (Federal Register, 1980) are given in Table 6.

Process Wastewater

Process wastewater is produced when reactors and filters are cleaned between dye syntheses. This cleanup water would contain unreacted intermediates, by-products, and dye. Other sources of wastewater from dye syntheses include floor washdown, laundry, workershowers (Keinath, 1976), and blowdown from scrubbers. Because there was no information on cleanup frequency and no data on the chemical content of cleanup waters, the loss of materials from equipment cleanup was not quantified.

Table 6

HAZARDOUS WASTES THAT MAY RESULT FROM ANTHRAQUINONE DYE AND PIGMENT PRODUCTION

Industry and EPA Hazardous Waste No.	Hazardous Waste	Hazard Code[a]
F002	The spent halogenated solvents,...chlorobenzene,...o-dichlorobenzene,...and the still bottoms from the recovery of these solvents.	T
F003	The spent **nonhalogenated** solvents, xylene, acetone,..., and the still bottoms from the recovery of these solvents.	I
F004	The spent **nonhalogenated** solvents,...nitrobenzene, and the still bottoms from the recovery of these solvents.	T
F005	The spent **nonhalogenated** solvents,...isobutanol, pyridine, and the still bottoms from the recovery of these solvents.	I,T

HAZARDOUS CHEMICALS USED IN THE MANUFACTURE OF ANTHRAQUINONE DYES AND PIGMENTS

Acetone	Naphthalene
Aniline	Nitrobenzene
p-Chloroaniline	Phenol
Chlorobenzene	Phthalic anhydride
1,2-Dibromoethane	Pyridine
1,2-Dichlorobenzene	Trichlorobenzenes
Dimethyl sulfate	Xylene
Isobutyl alcohol	

[a]EPA hazard code: Ignitable Waste (I) and Toxic Waste (T) (Federal Register, 1980)

Vapor Losses

Vapor losses to the environment are expected to be minimal. Many facilities have vents at the process vessels that lead to a scrubbing system (Keinath, 1976; DETO, 1980; Bradley and Kronowitt, 1954). The vapor losses to the scrubbing system were not quantified.

PRODUCT FILTRATION

Process Wastewater

The major contributors to potential discharges of material from filtration operations are the mother liquor and process wastewater from equipment washwaters. The mother liquor will contain unreacted intermediates, other by-products, and dye. Because the manufacture of anthraquinone dyes and pigments often involves organic solvents or reagents that do not become part of the dye molecule, the mother liquor may also contain significant amounts of organic material. In some cases the mother liquor may be an organic solvent. The concentration of material may be quite high in aqueous mother liquors. Keinath and Pollack (1978) analyzed two different batches (from the same manufacturer) of an aqueous mother liquor from the producton of the anthraquinone dye C.I. Acid Blue 25 (C.I. 62055). The results (in ppm) are shown below:

	Batch A	Batch B
Chloride	12,600	16,245
Suspended solids	26	2,097
Dissolved solids	112,000	112,880
Total solids	111,000	113,593
Volatile suspended solids	23	6,755
Chemical oxygen demand	41,855	34,656
Biological oxygen demand(BOD_5)	--	16,855
Total Kjeldahl nitrogen	--	1,755
Alkalinity	21,800	29,333

Thus the mother liquor from the manufacture of the same dye can vary from batch to batch even with the same manufacturer.

Mother liquors from the production of anthraquinone dyes are not usually treated before being discharged to the process wastewater; however, two methods of treatment have been evaluated that could substantially reduce the amount of organic material in the process wastewater, which, in turn, reduces the amount of organics on wastewater treatment solids. These two methods--wet-air oxidation and hyperfiltration--are discussed in a following section concerning wastewater treatment.

Solid Wastes

The solid wastes produced during product filtration are precipitated dye or insoluble pigment that are spilled during transfer of the press cake to the drying operation or remain as a residual in the filter press. These solid waste materials are assumed to be washed into the process wastewater system so that product filtration does not produce a solid waste directly, although solid wastes may result from wastewater treatment.

Vapor Losses

Vapor losses during filtration consist primarily of solvents and unreacted intermediates because the dye or pigment product and most of the by-products do not have significant vapor pressures. Many facilities have dust and vapor control systems that collect the material lost from materials handling, dye synthesis, and the filtration process (DETO, 1980; Keinath, 1976; Bradley and Kronowitt, 1954) and process it through a scrubber.

DRYING, GRINDING, STANDARDIZATION, BLENDING, AND PACKAGING

Solid Wastes

Solid wastes from the final processing or finishing of dyes and pigments consists principally of dusts produced during drying, grinding, standardization, blending, and packaging. Most of these dusts will be captured by moving air in a vent or hood system when they are used and would then be removed from the air in a baghouse. Bradley and Kronowitt (1954) detail the ventilation equipment at the Toms River, NJ, manufacturing facility which is an example of a facility with controls. The grinding and mixing of dry powders is done in a closed circuit. All powder loading, unloading, filling, and weighing is performed under hoods with exhausters and dust-controlling equipment.

Vapor Losses

There are two potential vapor emission sources in dye and pigment finishing. The drying operations, which remove mother liquor from the filter press cake, could also volatilize some of the unreacted intermediates, solvents, and by-products present. The vapors from product drying will be passed through a baghouse at most facilities, but very little condensation and removal of volatilized material is expected there even if significant cooling occurs because the large airflows will prevent vapor saturation. The second opportunity for chemicals to volatilize occurs if materials are carried from process to process in open tote boxes. However, very little volatilization is expected because of the low temperatures. Some of the organic vapors from open tote boxes will be entrained in air entering scrubbers or baghouses operated to control emissions at specific processing steps. If processed by a scrubber, the vapors will be collected and contribute to contamination of the process wastewater. If processed through a baghouse, the vapors will probably escape to the atmosphere.

WASTEWATER TREATMENT

Conventional Treatment

The principal potential source of emissions of dye, by-product, or intermediates to the environment from dye and pigment manufacturing operations is the aqueous process wastewater system. Each dye producer may have a different wastewater treatment system. Some producers discharge all process wastewaters directly to sewers and thus to publicly owned treatment works. Some producers have on-site wastewater treatment plants. These treatment plants are all site-specific designs with site-specific behavior. Several examples of on-site treatment facilities at dye production sites are discussed below to indicate the type of treatment often used and its effectiveness.

Bradley and Kronowitt (1954) described the Toms River, NJ, dye manufacturing facility that produces anthraquinone dyes and pigments. The plant wastewater treatment system consisted of an equalization pond, a neutralization step, a sedimentation basin, and an aeration basin followed by chlorination. Even though this is a 1954 reference, the treatment sequence reported is still typical of conventional treatment at chemical manufacturing facilities. No specifics were given regarding the quality of the effluent from treatment.

Games and Hites (1977) described a wastewater treatment system at a facility that manufactured anthraquinone dyes. It consisted of neutralization in an equalization pond (raw effluent was acidic), aeration in two lagoons (in series) that were mechanically stirred to accelerate aerobic biological degradation, and settling in two large ponds (containing 80% of the total system volume). The dye manufacturing facility processed an average of 11.4 million liters per day of wastewater. Total residence time (by volume) in the treatment system averaged 19 days, but sometimes because of flow patterns this was reduced to 6 days. The waste before treatment had a chemical oxygen demand (COD) of about 670 ppm. Treatment plant performance averaged about 70% and 80% reduction of COD and biological oxygen demand (BOD), respectively, to produce an effluent with a COD of 200 ppm and a BOD of 60 ppm. It is estimated that the daily discharge of organics in the treated water was 2200 kg.

Games and Hites identified and "semi-quantified" the dichloromethane-extractable compounds present in the dye plant raw wastewater and final effluent. Their study consisted of composite sampling over a 2.5-month period. Their results showed wide concentration variations between different composites, indicating that grab sampling techniques would have been misleading. Table 7 shows some of the compounds believed to be from anthraquinone dye production that were detected during the investigation and the concentration range at which they were detected.

Anliker and Clarke (1979) reported an effluent concentration before treatment from a dyestuff manufacturer as 900 to 4000 ppm BOD and 600 to 1000 ppm total organic carbon (TOC). Other documents (such as EPA, 1975) give wastewater flows at six different dye manufacturing plants as 33, 114, 175, 200, 800, and 1800 liters/kg finished product. Sampling of these wastestreams gave the following ranges: 200 to 5000 ppm BOD, 1200 to 4000 ppm COD, and 500 to 2000 ppm TOC.

Table 7

A PARTIAL LIST OF COMPOUNDS FOUND BY GAMES AND HITES (1977) IN THE COMPOSITE SAMPLES COLLECTED FROM A DYE MANUFACTURING PLANT

Compound	Raw Wastewater Concentration[a] (ppb)	Final Effluent Concentration[a] (ppb)
Aniline	36-480 (6)	10-96 (7)
_____, chloro-	ND[b]	7-12 (5)
_____, bromo-	3 (1)	ND
Anisidine (p-Methoxyaniline)	29-84 (2)	ND
Anthraquinone	49-110 (6)	ND
_____, amino-	69-160 (2)	5-29 (5)
_____, bromoaminohydroxy-	170-200 (2)	16-75 (3)
_____, dibromoamino-	92-170 (4)	ND
_____, dihydroxy-	ND	5-44 (3)
_____, hydroxy-	ND	5-8 (3)
_____, hydroxyamino-	ND	1.5-27 (4)
Chlorobenzene	90-530 (8)	ND
Dichlorobenzene	90-380 (8)	5-32 (3)
Nitrobenzene	15-240 (3)	23 (1)
Phenol	110-910 (8)	ND

[a]Number in parentheses refers to the total number of composites in which the compound was found. The raw effluent is based on eight total samples and the final effluent on nine total samples.

[b]None detected.

Several studies have dealt specifically with the effect of common wastewater treatment processes on dye production in wastewaters. Keinath and Pollack (1978) studied coagulation and flocculation using lime or ferric iron salts on wastewaters and found that only low organic removals (<40%) could be achieved. This probably reflects the fact that most dyes and their intermediates are water soluble. Tincher (1978) found that in the specific case of disperse dyes, larger organic removals were possible because the wastewater contained water-insoluble disperse dyes. Tincher also surveyed a river basin for organic contaminants from anthraquinone dyes used in carpet manufacturing. The maximum concentrations (ppb) he found are shown below:

	River Samples	Mud Samples
C.I. Disperse Red 55	187	119
C.I. Disperse Red 60	78	3400
C.I. Disperse Blue 7	239	1405
C.I. Acid Blue 25	502	550
C.I. Acid Blue 40	403	225

The presence of dye material in the mud shows some adsorption on the organic-inorganic matrix that makes up sediment because even the water-soluble acid dyes were present. These three studies taken together suggest that treatment by sedimentation either with or without added coagulants and sedimentation aids will result in waste solids that contain anthraquinone dyes and pigments. Neutralization with lime that results in calcium carbonate solids should also yield solids containing dyes and pigments that were present in the wastewater. The reagents, intermediates, and by-products from manufacturing will often be more soluble than the dyes and pigments because they are smaller molecules. However, they will still be partially adsorbed to solids generated during wastewater treatment.

Flege (1970) and Powell (1969) found that anthraquinone disperse dyes were only partially degraded in a simulated activated sludge aeration basin. C.I. Disperse Red 15 was converted to its leuco or enol form. C.I. Disperse Blue 7 was 60% converted to a comparable but more polar dye. Two dyes listed in Table 2 were also studied: C.I. Disperse Blue 3 and C.I. Disperse Violet 1 were 10% degraded after 15 days in aeration jars (25 ppm original concentration).

Tincher (1978) measured the concentrations of several anthraquinone dyes in the effluent from a treatment plant with an activated sludge treatment system. The maximum concentrations (in ppb) are shown below:

C.I. Disperse Red 55	3
C.I. Disperse Red 60	5.5
C.I. Acid Blue 25	214
C.I. Acid Blue 40	178

A bench-scale activated sludge system achieved better than 60% removal of the disperse dyes. However, the mechanism of removal was probably adsorption on the sludge rather than true biological oxidation. This conclusion was also reached by Flege (1970).

Several investigators (Flege, 1970; Powell, 1969; Little and Chillngworth, 1974; Brown et al., 1981) found anthraquinone dyestuffs were nontoxic or very mildly toxic to the aerobic wastewater bacteria.

Hunter (1973) evaluated the effects of six anthraquinone dyes on typical aerobic biological treatment systems such as activated sludge. After acclimatization of the microorganisms, four of dyes exhibited inhibition of biological oxidation:

C.I. 61505	Disperse Blue 3
C.I. 61570	Acid Green 25
C.I. 62500	Disperse Blue 7
C.I. 69500	Vat Green 3

C.I. Acid Blue 25 (C.I. 62055) and C.I. Vat Blue 6 (C.I. 69825) had no inhibitory effect after acclimatization.

The studies of biological treatment are interpreted as meaning that during treatment some of the dye and pigments are degraded and some are adsorbed onto the biological solids. The overall treatment effectiveness may be quite high. Games and Hites (1977) provided some data on the fate of some of the reagents, intermediates, and by-products during biological treatment. It is probably most conservative to assume that many are partially degraded, but that the biological treatment solids will contain small amounts of these compounds in the adsorbed state.

Several advanced or tertiary wastewater treatment processes have been studied to determine their effectiveness in treating dye plant process wastewaters. These processes include activated carbon adsorption, ozonation, irradiation, and wet-air oxidation, and hyperfiltration. A brief discussion of these advanced treatment processes follows.

Activated Carbon Adsorption

Granular activated carbon is extremely effective for removing color, conventional pollutants, and priority pollutants from dyestuff manufacture wastewaters. Because raw dyestuff wastewaters are characterized by high concentrations of carbonaceous materials, carbon exhaustion rates are high-->500 kg per 1000 m^3 wastewater processed (Keinath and Pollack, 1978). Therefore, from an economic viewpoint, carbon adsorption is best suited as a tertiary process.

Kitchens et al. (1978) described a wastewater facility that used activated carbon for tertiary treatment. The facilities were for the composite wastewaters from production of pyrotechnics at the Pine Bluff Arsenal in Arkansas. Several million pounds of anthraquinone dyes are used each year in the production of smokes, flares, and other pyrotechnics. Some of the anthraquinone dyes used included benzanthrone, 1,4-diamino-2,3-dihydroanthraquinone, 1,4-bis(p-toluidine)anthraquinone (C.I. Solvent Green 3, C.I. 61565), 1-methylaminoanthraquinone (C.I. Solvent Red 111 or C.I. Disperse

Red 9, C.I. 60505), and dibenzo[B,Def]chrysene-7,14-dione (C.I. Vat Yellow 4, C.I. 59100). In the treatment facilities the wastewater was neutralized with lime to an adjusted pH of ~ 11, and then sent on to two clarifying lagoons. The overflow from these lagoons then received a final pH adjustment. Heavy metals were precipitated by the addition of sulfides. Residual organics were removed by activated carbon. The pilot plant studies of this system indicated that treatment should remove far more than 99% of the contaminants.

Ozonation

Keinath and Pollack (1978) also studied ozonation as a treatment technology. They found reasonable reductions of organic carbon in raw dyestuff wastewaters could be obtained by ozonation, but only at extremely high ozone application levels (5 to 10 g ozone applied per g COD originally present; 1.6 g ozone applied per liter of treated wastewater). These high levels are likely to be economically infeasible.

Irradiation

Several investigators have studied the removal of organics from dye-containing wastewater using radiation (Craft and Eichholz, 1973; Piccinini and Ferrero, 1975; Gilbert, 1976; Hashimoto et al., 1979). The best utilization of the energy supplied by gamma radiation is the treatment of concentrated solutions of dyes at low doses with proper aeration. The chemical properties of products showed evidence of degradation of the aromatic ring system as well as simple decolorization. Some reduction in COD and BOD was reported, but the major benefit was color reduction.

Wet-Air Oxidation

Keinath and Pollack (1978) found that wet-air oxidation (oxidation at temperatures near 250°C) removed 86% of the chemical oxygen demand. Wet-air oxidation also reduced the concentrations of solvents, such as dichlorobenzene and nitrobenzene, to below detection limits.

Hyperfiltration

Hyperfiltration (a reverse osmosis process using a membrane that is permeable to small molecules) removed 90% of the color in mother liquors (Keinath and Pollack, 1978), but probably not substantial amounts of solvent molecules because they would be small enough to pass through the membrane. Gaddis et al. (1979) reported experiments in which 90 to 99% of the color was removed. With hyperfiltration, the treated mother liquor could be discharged to the process sewer, but the small-volume stream that retains the large dye and intermediate molecules would require special handling because of the high concentration of organics in it.

If these advanced technologies were practiced, they could have a significant impact on the amount of potentially hazardous material in plant wastewaters as well as reducing the amount of potentially hazardous material on wastewater treatment solids. Carbon adsorption may find applications; however, the other methods are probably too expensive.

SECTION 6

MATERIAL IN THE WASTE STREAMS FROM ANTHRAQUINONE DYE AND PIGMENT PRODUCTION

An in-depth discussion of the waste emissions from the anthraquinone dye and pigment industry would be incomplete when restricted to public sources of information and would also be complicated. First, there are 54 dyes and pigments of the 145 commercially significant dyes and pigments listed in Table 1 for which there are no Colour Index number, no structure known, and no process description given. There are 17 dyes and pigments that have been assigned a C.I. number, but no process information is available. Therefore there are 71 anthraquinone dyes and pigments for which no information is available regarding intermediates and other materials of production. Five of these 71 dyes are included in the 18 dyes and pigments known to be produced in amounts greater than 20 metric tons per year (listed in Table 2). Thus, there is no publically available process chemistry information for almost half of the anthraquinone dyes and pigments. Adding to the complications, the process chemistry of the other anthraquinone dyes and pigments often entails several different processes (sometimes as many as five) to achieve the same final product. It was not possible to estimate what percentage of the anthraquinone dye and pigment production uses which particular process. A quantitative estimate of the intermediates and by-products in the solid and aqueous waste streams from manufacturing was not attempted because we did not have access to the required proprietary information.

Table 8 summarizes the known intermediates and other organic chemicals used in the production of the 18 anthraquinone dyes and pigments with known production greater than 20 metric tons in 1978. These intermediates and other organics were identified from information in the Colour Index and BIOS reports (BIOS, 1945a,b,c). The dyes and pigments are listed in order of their production volume. The letter codes that identify the producers of each dye are defined in Table 9. Table 10 lists the manufacturers of the 145 commercially significant anthraquinone dyes and pigments, as well as the specific dyes and pigments produced by each manufacturer. The identity and corporate ownership of the producers is based on 1978 information. Since then, several dye production facilities or dye lines were sold. Sales that were announced in trade journals are shown as footnotes to Tables 9 and 10. A systematic search was not made to verify that all such sales have been listed, so the tables may not be complete.

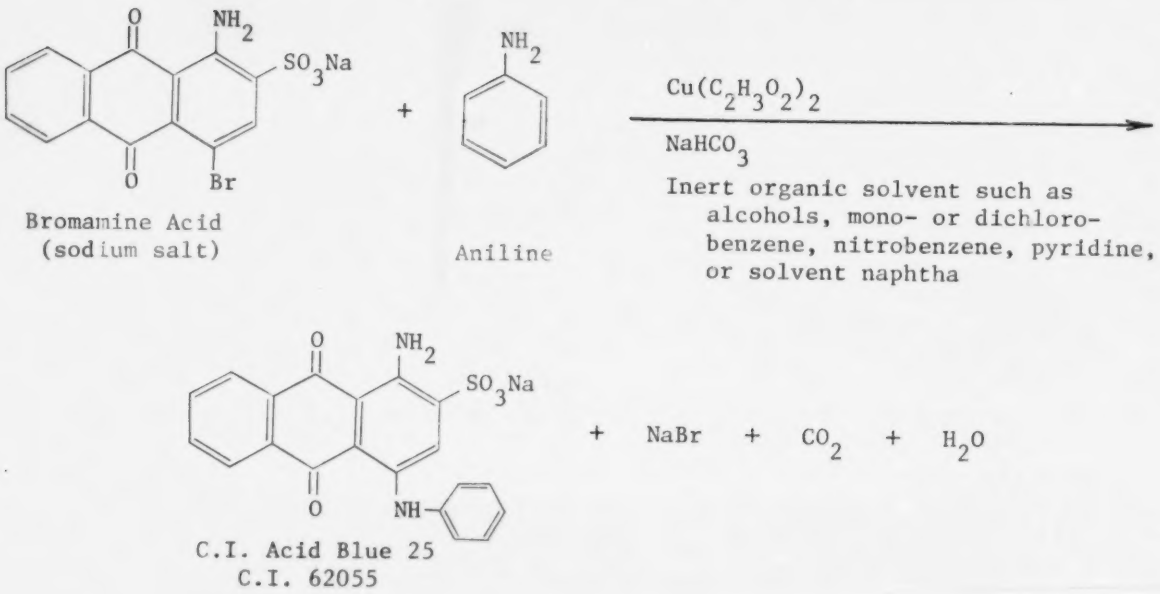
Table 8 does not identify other process chemistry by-products that are likely to be present. These include isomers of required intermediates (i.e., when hydroxy derivatives are formed the substitutions are not 100% directed to

the required positions) and the reaction products of these with the other intermediates and reagents used in the process. An investigation of these by-products was not within the scope of this study. All the intermediates and reagents listed in Table 8 will probably be present in the wastes from production of the dyes and pigments shown. Many of the substituted anthraquinones are produced using the catalytic action of metal catalysts, e.g., mercury and copper salts. These metals will also contaminate the process stream and therefore the waste streams. Dacre et al. (1979) confirm the presence of mercury as an impurity in the dye 1,4-di-p-toluidinoanthraquinone (C.I. Solvent Green 3, C.I. 61565). Mercury salts are required to produce the sulfonic acid intermediates for this dye. In another dye, 1-methylaminoanthraquinone (C.I. Solvent Red 111, C.I. 60505), mercury and copper were identified as impurities, along with anthracene and its dimethylamino derivatives (Dacre et al., 1979). The anthracene probably came as an impurity in anthraquinone manufactured by oxidation of anthracene.

Keinath and Pollack (1978) discussed various impurities found in the mother liquor filter washings of C.I. Acid Blue 25 (C.I. 62055). They detected in two different shipments the following priority pollutants that the producer suggested might be present:

	Concentration in ppm	
	Shipment A	Shipment B
Toluene	0.97	None detected
Nitrobenzene	16.9	7.38
Dichlorobenzene	26.1	Chromatographic peak interference
Dimethyl phthalate	0.97	None detected
Diethyl phthalate	23.3	Trace
Dibutyl phthalate	2.3	2.29

The presence of some of these impurities can be explained by an analysis of the process chemistry of C.I. Acid Blue 25 as shown below. Bromamine acid is reacted with aniline in an inert solvent that could include mono- and dichloro-benzene, nitrobenzene, pyridine, solvent naptha, or alcohol. The phthalates detected are probably the result of phthalic anhydride impurities in the anthraquinone intermediate reacting with the alcoholic solvents. Anthraquinone and its substituted derivatives are commonly produced by the Friedel-Crafts reaction between phthalic anhydride and substituted benzenes. If the reaction is not 100% complete, both will be found in the product.



The findings of Keinath and Pollack confirm the presence of organic solvents in the mother liquor as postulated in Section 5. Table 11 summarizes the various organic solvents used in the anthraquinone dye and pigment industry and the dyes and pigments known to use these solvents in their manufacturing process.

Table 8

ORGANIC MATERIALS THAT MAY APPEAR IN THE WASTE STREAMS FROM THE PRODUCTION OF ANTHRAQUINONE DYES AND PIGMENTS OF KNOWN 1978 U.S. COMMERCIAL PRODUCTION
> 20 metric tons

1978 U.S. Commercial Producers[a]	C.I. No.	C.I. Name	1978 U.S. Commercial Production (metric tons/yr)	Potential Organic Materials Released to the Environment
AC ACY DUP TRC	69525	Vat Black 25	1036	C.I. Vat Black 25 1-Aminoanthraquinone Benzanthrone (7H-Benz[de]anthracene-7-one) 3,9-Dibromobenzanthrone Isobutyl alcohol Naphthalene Sodium acetate Sodium carbonate
AC BAS DUP EKT TRC VPC	60756	Disperse Red 60	656	C.I. Disperse Red 60 1-Amino-2-bromo-4-hydroxyanthraquinone Phenol
AC ALT EKT HSH TRC	61505	Disperse Blue 3	630	C.I. Disperse Blue 3 1,4-Bis(2-hydroxyethylamino)anthraquinone 1,4-Bis(methylamino)anthraquinone 1-Bromo-4-methylaminoanthraquinone Copper acetate Ethanolamine Isobutanol Leuco-quinizarin Methylamine Piperidine (Hexahydropyridine) Quinizarin (1,4-Dihydroxyanthraquinone) Sodium carbonate
ACY BAS TRC	69825	Vat Blue 6	495	C.I. Vat Blue 6 2-Amino-1-bromo-3-chloroanthraquinone 2-Amino-3-chloroanthraquinone 2-Amino-1,3-dichloroanthraquinone Benzoyl chloride Chlorobenzene Chlorobenzoylbenzoic acid Indanthrone (6,15-Dihydro-5,9,14,18-anthrazinetetrone) Nitrobenzene 2-Nitro-3-chloroanthraquinone Phthalic anhydride

Table 8 (Continued)

1978 U.S. Commercial Producers	C.I. No.	C.I. Name	1978 U.S. Commercial Production (metric tons/yr)	Potential Organic Materials Released to the Environment
ATL BAS BDO DUP GAF ICI TRC VPC	62125	Acid Blue 40	408	C.I. Acid Blue 40 p-Aminoacetanilide 1-Amino-4-bromo-2-anthraquinonesulfonic acid
AC ACY DUP TRC	69500	Vat Green 3	393	C.I. Vat Green 3 1-Aminoanthraquinone 3-Bromobenzanthrone Isobutyl alcohol Naphthalene Sodium carbonate
ACY BAS TRC	59705	Vat Orange 2	335	C.I. Vat Orange 2 Pyranthrone
AC DUP EKT TRC	--	Disperse Blue 64	294	C.I. Disperse Blue 64 Unknown
DUP TRC VPC	--	Disperse Red 55	254	C.I. Disperse Red 54 Unknown
ALT BAS EKT TRC	62175	Disperse Red 86	150	C.I. Disperse Red 86 Unknown
AC ACY TRC VPC	69015	Vat Brown 3	108	C.I. Vat Brown 3 1-Aminoanthraquinone 1-Amino-4-benzoylaminoanthraquinone 1-Benzoylamino-4-chloroanthraquinone Benzoyl chloride 1,5-Diaminoanthraquinone Nitrobenzene Sodium acetate Sodium carbonate

Table 8 (Concluded)

1978 U.S. Commercial Producers	C.I. No.	C.I. Name	1978 U.S. Commercial Production (metric tons/yr)	Potential Organic Materials Released to the Environment
ACY TRC VPC	69025	Vat Orange 15	80	C.I. Vat Orange 15 1-Amino-5-benzoylaminoanthraquinone 1-Anthraquinonesulfonic acid, potassium salt Benzoyl chloride 1-Chloro-5-aminoanthraquinone 1-Chloro-5-benzoylaminoanthraquinone 1-Chloro-5-nitroanthraquinone 1,5-Diaminoanthraquinone o-Dichlorobenzene 5-Nitro-1-anthraquinonesulfonic acid Nitrobenzene Sodium acetate Sodium carbonate
HPC HRC HSH KON MRX UHL	58055	Pigment Violet 5:1	46	C.I. Pigment Violet 5:1 Quinazarin (1,4-Dihydroxyanthraquinone)
BAS GAF TRC	60755	Disperse Red 4	35	C.I. Disperse Red 4 Acetone 4-Aminoxanthopurpurin Dimethyl sulfate
HPC HSH KON MRX UHL	58000	Pigment Red 83	33	C.I. Pigment Red 83 Anthraquinone 2-Anthraquinonesulfonic acid 2-Chloroanthraquinone 1,2-Dibromoanthraquinone 2-Methylanthraquinone m-Nitro derivatives of anthracene
BAS DUP GAF	--	Disperse Red 59	29	C.I. Disperse Red 59 Unknown
AC ACY DUP EKT	60724	Disperse Violet 27	23	C.I. Disperse Violet 27 Unknown
AC ALT BAS HSH TRC	61100	Disperse Violet 1	23	C.I. Disperse Violet 1 o-Dichlorobenzene Leuco-1,4-diaminoanthraquinone Nitrobenzene Quinizarin (1,4-Dihydroxyanthraquinone)

[a]See Table 9 for explanation of code.

Table 9

DIRECTORY OF DYE AND ORGANIC PIGMENT MANUFACTURERS, 1978

Names of manufacturers that reported production and/or sales of anthraquinone dyes and pigments to the U.S. International Trade Commission for 1978 are listed below in order of their identification codes as used in Table 8.

Code	Name of Company	Code	Name of Company
Dye Manufacturers			
AC	American Color & Chemical Corp.	GAF[b]	GAF Corp.
ACY	American Cyanamid Co.	HSH	Harshaw Chemical Co.
ALT	Crompton & Knowles Corp., Dyes & Chemical Div.	HST	American Hoechst Corp. Industrial Chemicals Div.
ATL	Atlantic Chemical Corp.	ICI	ICI Americas, Inc., Chemical Specialties Co.
BAS	BASF Wyandotte Corp.	KON	H. Kohnstamm & Co., Inc.
BCC	Buffalo Color Corp.	MRT	Morton Norwich Products Inc., Morton Chemical Co. Div.
BDO	Benzenoid Organics, Inc.	SDC	Martin-Marietta Corp., Sodyeco Div.
DSC	Dye Specialties, Inc.	TRC	Toms River Chemical Corp.
DUP[a]	E.I. duPont de Nemours & Co., Inc.	VPC	Mobay Chemical Corp., Verona Dyestuffs Div.
EKT	Eastman Kodak Co., Tennessee Eastman Co. Div.		
Pigment Manufacturers			
ACY	American Cyanamid Co.	HSC[c]	Chemetron Corp., Pigments Div., Sub. of Allegheny Ludlum Industries, Inc.
CGY	Ciba-Geigy Corp.	HSH	Harshaw Chemical Co.
DUP[a]	E.I. duPont de Nemours & Co., Inc.	KON	H. Kohnstamm & Co., Inc.
HPC	Hercules, Inc.	MRX	Max Marx Color & Chemical Co.
HRC	Harmon Colors Corp.	UHL	Paul Uhlich & Co., Inc.

[a] In 1979 duPont sold its paper dye operations to Mobay Chemical Corp., its textile dye operations to Ciba-Geigy Corp. and Crompton & Knowles Corp., and its ink dye operations to Morton Norwich Products Inc., Morton Chemical Co. Division.

[b] In 1978 GAF Corp. sold its dye operations to BASF Wyandotte Corp.

[c] In 1978 Chemetron Corp. sold its dye and pigment operations to BASF Wyandotte Corp.

Table 10

1978 PRODUCERS OF ANTHRAQUINONE DYES AND PIGMENTS

C.I. No.	C.I. Name
American Color & Chemical Corp.	
59815	Vat Blue 18
60505	Solvent Red 111
60724	Disperse Violet 27
60756	Disperse Red 60
61100	Solvent Violet 11
61100	Disperse Violet 1
61505	Disperse Blue 3
61551	Disperse Blue 134
61551	Solvent Blue 36
61552	Solvent Blue 59
62015	Disperse Red 11
62015	Solvent Violet 26
62500	Disperse Blue 7
62500	Solvent Blue 69
67300	Vat Yellow 2
69015	Vat Brown 3
69015	Pigment Brown 28
69500	Vat Green 3
69525	Vat Black 25
71120	Vat Brown 14
-	Disperse Blue 64
-	Solvent Blue 16
-	Vat Black 14

C.I. No.	C.I. Name
American Cyanamid Co.	
58000	Mordant Red 11
58000	Pigment Red 83
59700	Vat Orange 9
59700	Pigment Orange 40
59705	Vat Orange 2
59800	Vat Blue 20
59800	Pigment Blue 65
59815	Vat Blue 18
59825	Vat Green 1
59850	Vat Green 9
60505	Solvent Red 111
60724	Disperse Violet 27
61552	Solvent Blue 59
61565	Solvent Green 3
63265	Disperse Blue 73
69005	Vat Black 27
69015	Vat Brown 3
69015	Pigment Brown 28
69025	Vat Orange 15
69500	Vat Green 3
69525	Vat Black 25
69825	Vat Blue 6
69825	Pigment Blue 64
70800	Vat Brown 1
-	Solvent Blue 58
-	Vat Black 21

Table 10 (Continued)

C.I. No.	C.I. Name
American Cyanamid Co. (cont.)	
-	Vat Black 22
-	Vat Yellow 15
Crompton & Knowles Corp., Dyes & Chemical Div.	
60710	Disperse Red 15
60710	Solvent Red 53
61100	Solvent Violet 11
61100	Disperse Violet 1
61505	Disperse Blue 3
62070	Acid Blue 145
62175	Disperse Red 86
Atlantic Chemical Corp.	
60505	Disperse Red 9
61530	Acid Blue 27
62055	Acid Blue 25
62125	Acid Blue 40
62130	Acid Blue 41
BASF Wyandotte Corp.	
59705	Vat Orange 2
59805	Vat Blue 19
59825	Vat Green 1
59850	Vat Green 9
60755	Disperse Red 4
60756	Disperse Red 60
61100	Solvent Violet 11
61100	Disperse Violet 1
61530	Acid Blue 27
BASF Wyandotte Corp. (cont.)	
61570	Acid Green 25
61570	Acid Green 95
62015	Disperse Red 11
62125	Acid Blue 40
62175	Disperse Red 86
67000	Vat Red 10
68700	Vat Violet 13
69825	Vat Blue 6
69825	Pigment Blue 64
71135	Vat Red 32
71135	Pigment Red 189
71200	Vat Blue 16
-	Basic Blue 60
-	Disperse Blue 87
-	Disperse Red 59
-	Disperse Red 91
-	Disperse Red 92
-	Disperse Red 263
-	Vat Blue 66
Buffalo Color Corp.	
59855	Vat Black 16
61570	Acid Green 25
61570	Acid Green 95

Table 10 (Continued)

C.I. No.	C.I. Name
Benzenoid Organics, Inc.	
61525	Solvent Blue 11
61530	Acid Blue 27
61570	Acid Green 25
61570	Acid Green 95
62045	Acid Blue 62
62105	Acid Blue 78
62125	Acid Blue 40
Ciba-Geigy Corp.	
65300	Pigment Red 177
Dye Specialties, Inc.	
61565	Solvent Green 3
E.I. duPont de Nemours & Co., Inc.[a]	
59710	Vat Orange 4
59825	Vat Green 1
60010	Vat Violet 1
60010	Pigment Violet 31
60724	Disperse Violet 27
60756	Disperse Red 60
61102	Disperse Violet 28
61512	Basic Blue 22
61570	Acid Green 25
61570	Acid Green 95
62055	Acid Blue 25
62073	Acid Blue 230
62125	Acid Blue 40
69005	Vat Black 27
69500	Vat Green 3
69525	Vat Black 25
69810	Vat Blue 14
69810	Pigment Blue 22
70800	Vat Brown 1
71050	Vat Green 8
71135	Vat Red 32
71135	Pigment Red 189
-	Acid Blue 298
-	Basic Blue 21
-	Basic Blue 35
-	Basic Blue 94
-	Disperse Blue 60
-	Disperse Blue 62
-	Disperse Blue 64
-	Disperse Blue 77
-	Disperse Blue 109
-	Disperse Blue 192
-	Disperse Green 7
-	Disperse Red 55
-	Disperse Red 59
-	Disperse Red 217
-	Disperse Violet 17
-	Disperse Violet 26
-	Disperse Violet 64
-	Vat Yellow 22
Eastman Kodak Co., Tennessee Eastman Co. Div.	
60724	Disperse Violet 27
60756	Disperse Red 60
60767	Disperse Blue 27

Table 10 (Continued)

C.I. No.	C.I. Name
Eastman Kodak Co., (cont.)	
61505	Disperse Blue 3
62175	Disperse Red 86
-	Disperse Blue 62
-	Disperse Blue 64
-	Disperse Blue 77
-	Disperse Blue 112
-	Disperse Blue 118
-	Disperse Red 138
-	Disperse Violet 41
GAF Corp. [b]	
60755	Disperse Red 4
62125	Acid Blue 40
-	Basic Blue 60
-	Disperse Red 59
-	Disperse Red 263
Hercules, Inc.	
58000	Mordant Red 11
58000	Pigment Red 83
58055	Pigment Violet 5:1
Harmon Colors Corp.	
58055	Pigment Violet 5:1
59300	Pigment Red 168
69810	Vat Blue 14
69810	Pigment Blue 22
70600	Pigment Yellow 24
71105	Pigment Orange 43
71127	Pigment Red 224

C.I. No.	C.I. Name
Harmon Colors Corp. (cont.)	
71130	Vat Red 23
71130	Pigment Red 179
71140	Vat Red 29
71140	Pigment Red 190
71145	Pigment Red 123
Chemetron Corp., Pigments Div., Sub. of Allegheny Ludlum Industries, Inc. [c]	
71140	Vat Red 29
71140	Pigment Red 190
71145	Pigment Red 123
Harshaw Chemical Co.	
58000	Mordant Red 11
58000	Pigment Red 83
58055	Pigment Violet 5:1
60710	Disperse Red 15
60710	Solvent Red 53
60730	Acid Violet 43
61100	Solvent Violet 11
61100	Disperse Violet 1
61505	Disperse Blue 3
61570	Acid Green 25
61570	Acid Green 95
62055	Acid Blue 25
62070	Acid Blue 145
63615	Mordant Black 13

Table 10 (Continued)

C.I. No.	C.I. Name
American Hoechst Corp., Industrial Chemicals Div.	
59100	Vat Yellow 4
59105	Vat Orange 1
59300	Pigment Red 168
59300	Vat Orange 3
61200	Reactive Blue 19
71100	Vat Red 15
71100	Pigment Red 194
71105	Vat Orange 7
71105	Pigment Orange 43
71110	Vat Red 14
71137	Pigment Red 149
-	Disperse Blue 95
ICI Americas, Inc., Chemical Specialties Co.	
61205	Reactive Blue 4
61205:1	Reactive Blue 5
62055	Acid Blue 25
62125	Acid Blue 40
62130	Acid Blue 41
H. Kohnstamm & Co., Inc.	
58000	Mordant Red 11
58000	Pigment Red 83
58055	Pigment Violet 5:1
60730	Acid Violet 43
61565	Solvent Green 3
61570	Acid Green 25
61570	Acid Green 95
Morton Norwich Products Inc., Morton Chemical Co. Div.	
61551	Disperse Blue 134
61551	Solvent Blue 36
61554	Solvent Blue 35
61705	Solvent Violet 14
-	Solvent Blue 98
-	Solvent Red 168
Max Marx Color & Chemical Co.	
58000	Mordant Red 11
58000	Pigment Red 83
58055	Pigment Violet 5:1
Martin-Marietta Corp., Sodyeco Div.	
58825	Vat Green 7
-	Disperse Violet 36
-	Disperse Violet 81
Toms River Chemical Corp.	
59105	Vat Orange 1
59700	Vat Orange 9
59700	Pigment Orange 40
59705	Vat Orange 2
59800	Vat Blue 20
59800	Pigment Blue 65
59815	Vat Blue 18
59850	Vat Green 9
60005	Vat Violet 9
60005	Pigment Violet 33

Table 10 (Continued)

C.I. No.	C.I. Name
Toms River Chemical Corp. (cont.)	
60010	Vat Violet 1
60710	Disperse Red 15
60710	Solvent Red 53
60755	Disperse Red 4
60756	Disperse Red 60
61100	Solvent Violet 11
61100	Disperse Violet 1
61125	Acid Blue 23
61505	Disperse Blue 3
61570	Acid Green 25
61570	Acid Green 95
61585	Acid Blue 80
62055	Acid Blue 25
62105	Acid Blue 78
62125	Acid Blue 40
62175	Disperse Red 86
62500	Disperse Blue 7
62500	Solvent Blue 69
63000	Acid Blue 43
63010	Acid Blue 45
63265	Disperse Blue 73
65429	Vat Yellow 33
67300	Vat Yellow 2
68700	Vat Violet 13
69005	Vat Black 27
69015	Vat Brown 3
69015	Pigment Brown 28
69025	Vat Orange 15
69500	Vat Green 3
69525	Vat Black 25
69825	Vat Blue 6
69825	Pigment Blue 64
70320	Vat Red 13
70320	Pigment Red 195
70800	Vat Brown 1
71100	Vat Red 15
71100	Pigment Red 194
71105	Vat Orange 7
-	Acid Blue 277
-	Disperse Blue 55
-	Disperse Blue 64
-	Disperse Red 55
-	Disperse Red 178
-	Vat Black 22
-	Vat Brown 11
-	Vat Brown 13
Paul Uhlich & Co., Inc.	
58000	Mordant Red 11
58000	Pigment Red 83
58055	Pigment Violet 5:1
Mobay Chemical Corp., Verona Dyestuffs Div.	
59105	Vat Orange 1
60756	Disperse Red 60
61111	Basic Blue 47
62055	Acid Blue 25
62105	Acid Blue 78
62125	Acid Blue 40

Table 10 (Concluded)

C.I. No.	C.I. Name
Mobay Chemical Corp., Verona Dyestuffs Div. (cont.)	
62560	Acid Green 41
63285	Disperse Blue 56
6[illegible]300	Vat Yellow 2
69015	Vat Brown 3
69015	Pigment Brown 28
69025	Vat Orange 15
70150	Disperse Yellow 77
-	Basic Blue 45
-	Disperse Blue 81
-	Disperse Red 55
-	Disperse Red 133
-	Disperse Red 159
-	Reactive Blue 29
-	Vat Green 32
-	Vat Violet 21

[a] In 1979 duPont sold its paper dye operations to Mobay Chemical Corp., its textile dye operations to Ciba-Geigy Corp. and Crompton & Knowles Corp., and its ink dye operations to Morton Norwich Products Inc., Morton Chemical Co. Division.

[b] In 1978 GAF Corp. sold its dye operations to BASF Wyandotte Corp.

[c] In 1978 Chemetron Corp. sold all its dye and pigment operations to BASF Wyandotte Corp.

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Table 11

ORGANIC SOLVENTS USED IN ANTHRAQUINONE DYE AND PIGMENT MANUFACTURING AND THE DYES AND PIGMENTS KNOWN TO BE ASSOCIATED WITH THEIR USE

Solvent	C.I. No.	C.I. Name
Acetone	60755	Disperse Red 4[a]
Chlorobenzene	60005	Vat Violet 9/Pigment Violet 33
	60010	Vat Violet 1/Pigment Violet 31
	69825	Vat Blue 6[a]/Pigment Blue 64
o-Dichlorobenzene	59700	Vat Orange 9/Pigment Orange 40
	61100	Disperse Violet 1[a]/Solvent Violet 11
	69025	Vat Orange 15[a]
Ethanol	62500	Disperse Blue 7/Solvent Blue 69
	69800	Pigment Blue 60/Vat Blue 4
	71105	Vat Orange 7/Pigment Orange 43
Isobutanol	59700	Vat Orange 9/Pigment Orange 40
	59825	Vat Green 1
	60005	Vat Violet 9/Pigment Violet 33
	60010	Vat Violet 1/Pigment Violet 31
	61505	Disperse Blue 3[a]
	69500	Vat Green 3[a]
	69525	Vat Black 25[a]
	70320	Vat Red 13/Pigment Red 195
Naphthalene	67300	Vat Yellow 2
	69500	Vat Green 3[a]
	69525	Vat Black 25[a]
Nitrobenzene	59710	Vat Orange 4/Pigment Red 216
	59800	Vat Blue 20/Pigment Blue 65
	59805	Vat Blue 19
	59825	Vat Green 1
	60005	Vat Violet 9/Pigment Violet 33
	60010	Vat Violet 1/Pigment Violet 31
	61100	Dispere Violet 1[a]/Solvent Violet 11
	68700	Vat Violet 13
	69015	Vat Brown 3[a]/Pigment Brown 28
	69025	Vat Orange 15[a]
	69825	Vat Blue 6[a]/Pigment Blue 64
	70600	Vat Yellow 1/Pigment Yellow 24
	71050	Vat Green 8
Phenol	62055	Acid Blue 25

Table 11 (Concluded)

Pyridine	59700	Vat Orange 9/Pigment Orange 40
	70800	Vat Brown 1
	71100	Vat Red 15/Pigment Red 194
	71105	Vat Orange 7/Pigment Orange 43
	71110	Vat Red 14
Xylene	60005	Vat Violet 9/Pigment Violet 33

[a]Major anthraquinone dye or pigment with a known production greater than 20 metric tons in 1978 listed in Table 2.

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